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Evaluation of Emerging Technologies for the Destruction of Hazardous Wastes

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The objective of this report is to provide detailed information regarding four innovative alternative technologies demonstration projects for treating and destroying hazardous wastes. Under a cooperative agreement between the U.S. Environmental Protection Agency and the State of California, the Department of Health Services (DHS) carried out a pilot scale test program on the following promising technologies.

1. High Temperature Fluid-Wall — Thagard Research
2. Evaluation of Emission Tests from SunOhio Mobile Treatment Process — Air Resources Board, State of California
3. Wet Air Oxidation — Zimpro
4. Evaluation of Emission Tests from Wet Air Oxidation Zimpro Process — Air Resources Board, State of California

Discussions of the above processes include project descriptions, results, conclusions, and recommendations.

This report was submitted in partial fulfillment of Cooperative Agreement No. R-808908 under sponsorship of the U.S. EPA and the State of California, DHS.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report discusses the evaluation of several alternative technologies for treating hazardous wastes. The information contained in this report will be useful to those within the public and private sector responsible for the management of hazardous wastes.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

David G. Stephan
Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

The objective of this report is to provide detailed information regarding four innovative alternative technologies demonstration projects for treating and destroying hazardous wastes. Under a cooperative agreement between the U. S. EPA and the State of California, the Department of Health Services (DHS) carried out a pilot scale test program on the following promising technologies.

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SECTION 1

INTRODUCTION

On January 20, 1981, the State of California entered into a cooperative agreement with the Office of Research and Development, U. S. EPA, to evaluate selected promising technologies for destroying hazardous waste using pilot scale test programs. This report summarizes detailed information such as process descriptions, results, and conclusions for each process studied. The mention of a process in the report should in no way be considered an endorsement of the process by either State of California or the U. S. EPA.

SECTION 2

HIGH TEMPERATURE FLUID-WALL, THAGARD RESEARCH COMPANY

SUMMARY

Four volatile chlorinated hydrocarbons, dichloromethane; 1,1,1-trichloroethane; carbon tetrachloride; and Freon-12 (dichlorodifluoromethane) and one nonvolatile chlorinated hydrocarbon (hexachlorobenzene) have been decomposed in the High Temperature Fluid-Wall (HTFW) Reactor in bench-scale tests to assess the applicability of the device for efficient destruction of these particular compounds.

The hexachlorobenzene, loaded onto a solid radiation target, exhibited high (< 99.9999 percent) destruction efficiency, while the vapors (which could be heated only by secondary thermal conduction from solid radiation target) exhibited destruction efficiencies related inversely to the compound heats of formation, indicating that vapor-phase reaction temperatures were lower than the solid reaction. Destruction efficiencies ranged from 99.999965 percent for dichloromethane to 84.99 percent for Freon-12. Heat transfer analysis indicated that vapor heating is dependent on the solid particle density, and that efficient heating (and destruction) of vapors can be achieved simply by increasing the particle density.

INTRODUCTION

HTFW Reactor

The HTFW Reactor was developed originally for the continuous dissociation of methane into carbon fines and hydrogen. This particular process required the generation of stable temperatures above 1,700°C and the prevention of precipitate formation on the reactor walls. This fact has particular relevance to the project herein.

To achieve both goals simultaneously, the reacting stream is kept out of physical contact with the reactor wall by means of a gaseous blanket formed by flowing an inert gas radially inward through the porous reactor tube (or core). Both high temperatures and high rates of heat transfer are achieved by heating the porous carbon core to incandescense so that the predominant mode of heat transfer is by radioactive coupling from the core to the stream.

A partial vertical cross section of a typical HTFW Reactor is shown in Figure 2–1, and a horizontal cross section is shown in Figure 2–2.

The reactor is heated electrically with six carbon resistance heaters. Because of the extreme temperatures encountered in operation of the device, the insulation package consists not of refractory brick but of a radiation shield made of multiple layers of graphite paper backed up with carbon felt.

The short residence time associated with the reactor which demands the pulverization of solid feeds also lends itself to a compact system where a reasonably high throughput is seen for a small installation, and portability becomes an attainable design feature. Thus, it is suggested that the HTFW Reactor can provide a practical solution to the problem of disposing of many multi-component toxic and hazardous wastes. Work done with the reactor prior to this effort on a variety of wastes, in addition to a wide range of chemical processing, has indicated that there was a potential for this technology in waste disposal.

The Experimental Program

In the subject program, volatile chlorinated hydrocarbons of low molecular weight were examined to identify and perhaps quantify the applicability of the reactor to this class of waste. These tests then represent an extension of previous work where solid and liquid chlorinated hydrocarbons loaded onto solid carriers were treated in the reactor with high destruction efficiencies.

The treatment of radiation-transparent vapors and gases in the HTFW Reactor involves *conductive* heating of the vapors in physical contact with a target solid which is being heated *radiatively* by the reactor, so the extremely rapid surface heating which is seen in destruction of materials loaded onto solids is not encountered and the *operating mechanisms differ in kind rather than just degree.*

A detailed computer analysis of the governing parameters of secondary heating of gases by radiatively-heated solids has been performed. The analysis gives rise to a conclusion that only a small gas "bubble" surrounding the particle is actually conductively heated to a high temperature and thus the governing parameter is actually the *number* of particles introduced into the reactor. This analysis had not been completed at the time of the actual experimentation, so the design of the experiments unfortunately could not take these factors into account. Thus, while the results are encouraging, they do not represent what a final process may accomplish.

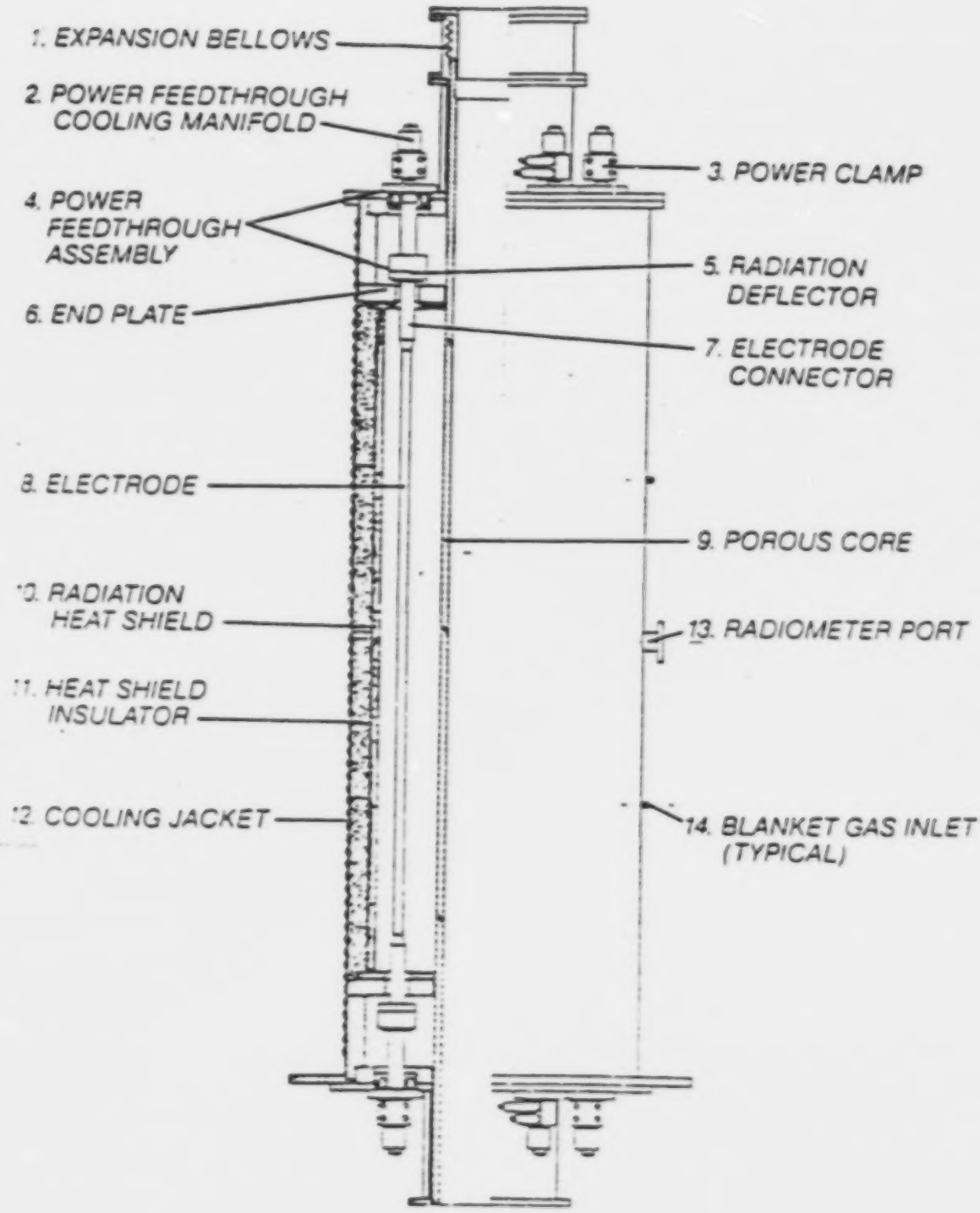

FIGURE 2-1: VERTICAL CROSS SECTION OF A TYPICAL HTFW REACTOR

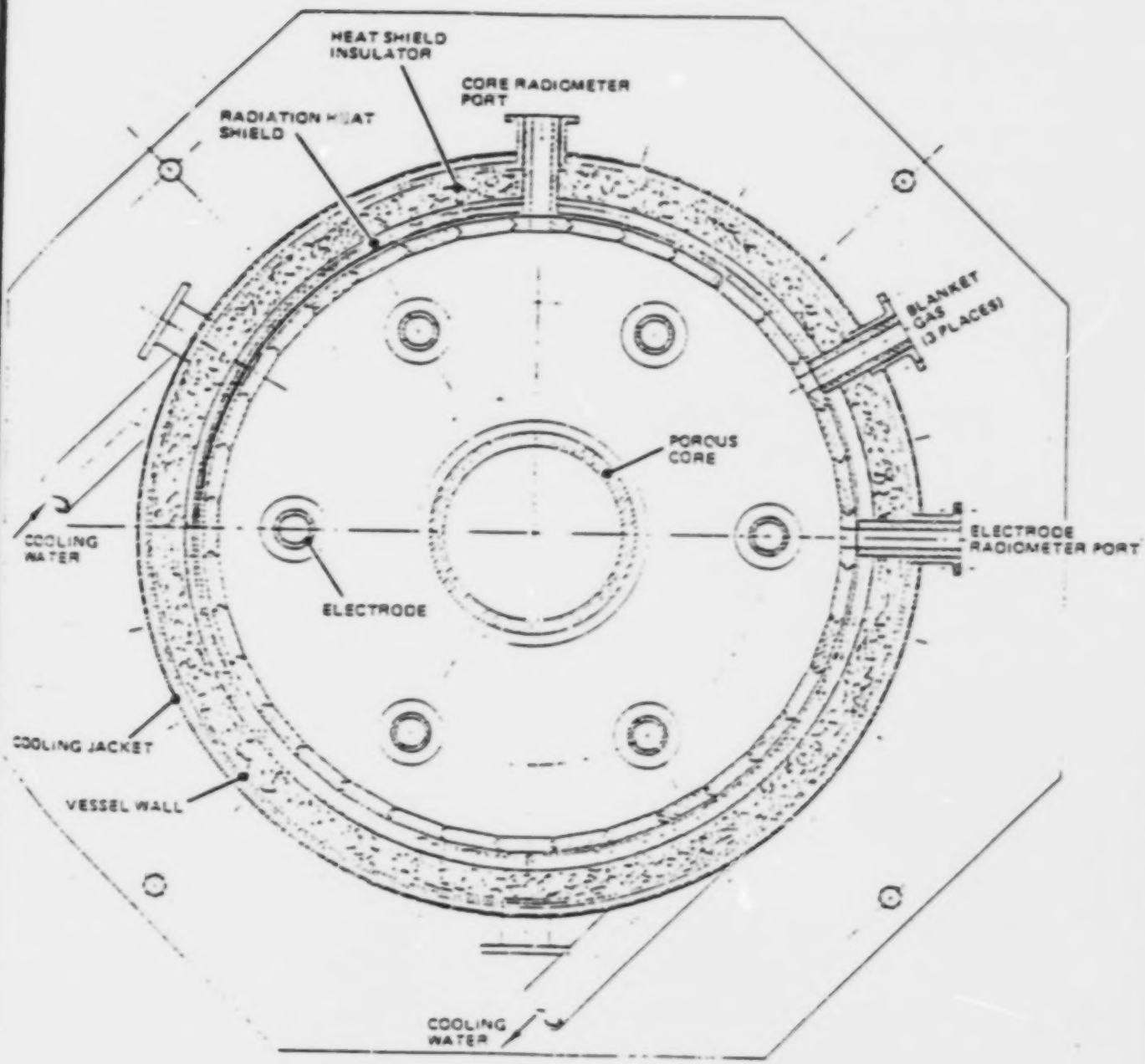

FIGURE 2-2: HORIZONTAL CROSS SECTION OF A HTFW REACTOR

RESULTS AND CONCLUSIONS

Chlorinated Hydrocarbon Vapor Samples

The most important conclusion we draw from the work completed is that chlorinated hydrocarbons introduced into the reactor *in the vapor form* are much more difficult to destroy than similar materials loaded onto solids, *given identical residence times and* reactor temperatures.

While the governing factor in the case of the solids was the direct absorption of radiation by the solid surfaces and consequent extremely rapid heating, the governing factor in the case of the vapors was the *conduction* of the heat from the particle surface into the vapor—a much slower process limited in rate by the *thermal conductivity* of the vapor itself.

Thus, as might be anticipated, the temperature levels achieved in the vapors for a given residence time will not, in general, be as high as the temperatures achieved on the solids. The experimental result of this behavior will be that minimum temperatures and minimum residence times for complete destruction of the vapor-phase substances will not be achieved, and that the observed destruction levels will now be critically dependent on the heat of formation of the substance being investigated.

This was graphically demonstrated in the tests performed as indicated in Table 2-1:

TABLE 2-1: CRITICAL FACTORS AND RESULTS IN VOLATILE CHLORINATED HYDROCARBON TREATMENT

MATERIAL	H_f, KCAL/MOLE	DESTRUCTION EFFICIENCY
Dichloromethane, CH_2C1_2	21.0	99.999965%
1,1,1-Trichloroethane, $CC1_3CH_3$	32 (est)	99.99278%
Carbon Tetrachloride, $CC1_4$	25.5	99.9756%
Freon-12, Dichloridifluoromethane, $CC1_2F_2$	94.0	84.99%

Chlorinated Hydrocarbons Solid Sample

The results for hexachlorobenzene (HCB) in soil are in agreement with HCB results on carbon, thus duplicating both the destruction and analytical methods and further substantiating the conclusion that the solids are rapidly heated and the toxic material effectively decomposed.

Despite some data problems, the fraction of HCB remaining on the solids and in the effluent gases was approximately 10^{-6}, corresponding to a destruction efficiency of approximately 99.9999 percent.

The demonstration of gettering of chlorine (from decomposition of HCB) with calcined lime (CaO) mixed with the soil produced no identifiable results. Since gettering of halogens and sulfur with lime and subsequent fixing into a vitreous slag has been previously demonstrated on numerous occasions with other materials we must conclude that some deficiency in the experimental procedure was introduced (inadequate mixing of the lime in the soil, too low a CaO/Cl ratio for this particular application, etc.). Subsequent experimental work will seek to quantify this parameter which is an important system consideration of on-site disposal.

Discussion of Analytical Results

Comparison of the analytical results from the principal laboratory (West Coast Technical Service [WCTS]) and the back-up laboratory (Rockwell) indicated poor agreement between the two sets. Therefore, we have based our conclusions (on destruction efficiencies) primarily on the WCTS results because of the greater number of samples analyzed by them and a much stronger indication of internal consistency for this particular set of experiments.

RECOMMENDATIONS

The bench-scale tests performed under this program utilized a general purpose three-inch HTFW Reactor and -100 mesh carbon granules as the radiation target material to provide heating of the chlorinated hydrocarbon vapors.

The results of destruction levels of these vapors are considerably poorer than results obtained by loading the hydrocarbon directly onto solids. However, the critical operational parameters relating to this behavior have been identified, and we believe that the destruction of vapors as such without formation of degradation products can be accomplished.

The first three recommendations below are directed at the problem of incomplete degradation of vapors.

The fourth recommendation is addressed at optimization of halogen gettering, while the fifth calls for a demonstration of a high level of destruction of chlorinated dioxins and dibenzofurans.

The last recommendation addresses the practical problem of mechanically introducing samples as completely dispersed powders.

1. Keeping the ratio of carbon to vapor a constant, the destruction efficiency should be measured as a function of the size of the carbon particles down to one micron, our prediction being that the smallest sizes, corresponding to higher particle density, will result in higher destruction efficiency.

2. Using the optimum particle size determined in No. 1 above, destruction efficiency should be measured as a function of the ratio of the weight of carbon to that of the vapor.

3. The optimum particle size and concentration (relative to the vapor) should then be tested with a variety of materials to assess the potential of the HTFW Reactor for direct destruction of vapors. Trichloroethane is suggested to test for formation of degradation by-products: Freon-12 would represent a difficult fully-halogenated material.

4. Gettering should be demonstrated and optimized using, for example, HCB on soil. The parameters to be varied will include particle size and stoichiometry.

5. A demonstration should be made of the efficient destruction of chlorinated dioxins and dibenzofurans. If possible, less toxic isomers can be used as surrogates to reduce hazards. Such a demonstration will be useful not only to qualify the HTFW Reactor for such specialized materials, but also demonstrate that they are not created in the reactor.

6. In addition to determining optimum particle size it is necessary to optimize the methods of introduction without allowing agglomeration. The present system is known to be far from optimum, although critical design parameters are identified and much existing machinery from the mining and food processing industries can be brought to bear on the problem.

BACKGROUND AND RELATED WORK

As mentioned in the introduction, the most generally acceptable methods for treatment of many hazardous materials involve high temperatures. The use of high temperatures to destroy chemical substances and to produce glasses has been standard practice for many years; however, practical process equipment operating much above 1200°C has generally encountered limitations in materials of construction. Most refractory liners either degrade mechanically or dissolve in the slags found in many waste streams. Another limitation occurs because of the inefficiency arising when

the process temperature approaches the effective flame temperature. Maintenance of pyrolysis or incineration equipment with moving parts in the high temperature region presents a potentially severe problem when uncharacterized feed materials with fusible species are introduced or precipitable products are formed.

In theory, the high temperature with the HTFW Reactor core should reduce samples to their simple molecular forms. The high rate of cooling prevent reformation of potentially hazardous recombination products, and the high rate of heating allows relatively large sampling rates at short residence times. Hydrocarbons are readily pyrolyzed to $C + H_2$; oxygen-bearing hydrocarbonaceous materials are gasified to $CO + H_2 + C$; halogenated organic compounds are decomposed to $C + Cl_2 + HCl$. In the last case, the addition of calcium hydroxide (or calcium oxide) results in the "gettering" of the chlorine to form $CaCl_2$. Inorganic compounds such as clay which melt below the reactor core temperature are fused into vitreous solids. Most metal salts, such as $CaCl_2$, are soluble in such molten glasses leaving vitrified beads with the salts locked up in solid solution.

Organic Compounds

In the absence of added secondary materials, organic compounds will be pyrolyzed to produce elemental or simple molecular forms of the starting materials, e.g., C, H_2HCl, or Cl_2 for chlorinated hydrocarbons.

In the presence of oxygen (air) they will be gasified to produce CO, H_2 and HCl.

In the presence of oxygen, H_2O and $Ca(OH)_2$, gasification will be accompanied by gettering of the chlorine. In the presence of soils or sediments, or if additional clay is added, the $CaCl_2$ can be locked up in an insoluble vitreous mass.

Hexachlorobenzene

A final report titled "A Feasibility Study of a High Temperature Fluid Wall Reactor (HTFWR)" was submitted to the Industrial Environmental Research Laboratory of EPA in Edison, New Jersey, in February 1981.* The primary objective of this feasibility program was to demonstrate that the surrogate material HCB is effectively degraded during passage through the HTFW Reactor operating

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* Work carried out under contract with Mason and Hanger.

under normal conditions. The reactor used was the six-inch prototype, designed and operated by Thagard Research Corporation at South Gate, California. HCB was selected as a surrogate both to avoid the difficulties of experimenting with hazardous materials such as polychlorinated biphenyls (PCBs) or Kepone, and to provide a substitute which is similar but which is know to be even more difficult to decompose.[1]

Measurements were carried out on October 23, October 30, and November 3, 1980. The experiments indicated that in excess of 99.9999 percent of the original material was destroyed for a core temperature of 2200°C (4000°F) and a residence time of approximately 0.1 second. Since HCB is known to have greater thermal stability than PCBs or Kepone, it is expected that the degradation efficiency for these hazardous materials would be at least as high as indicated for HCB.

PCB-Contaminated Sediment

In a recently concluded experimental program,** the HTFW Reactor was used to demonstrate destruction of PCBs in solids. Samples consisted of approximately 1 percent PCB as Aroclor 1242 in either fine soil for -100 mesh carbon. The conclusions reached were:

1. An overall reduction in concentration of PCB by a factor of 2.3×10^{-6} was achieved with a standard deviation of 0.8×10^{-6}. This corresponds to a destruction efficiency of 99.99972 percent.

2. Destruction was essentially similar for carbon and soil substrates, with slightly higher efficiencies for soil.

3. Destruction efficiency was essentially independent of feedrate in the 50–100 g/m range for the 3-inch reactor at 2343°C.

4. A 2:1 reduction in HCl was observed for a 2x stoichiometric addition of lime. The gettering factor was limited by the unexpected presence of sulfur in the soil with the resultant competition to form CaS.

** The program was carried out by Baird Corporation under agreement No. N256055ZKX with Rockwell International Corporation, Environmental and Monitoring Services. Rockwell, in turn, was operating under contract No. 68-03-3014 with the U. S. EPA.

1 R. A. Carnes "Thermal Degradation of Kepone" in the News of Environmental Research in Cincinnati, MERL, February 15, 1977.

While a high efficiency of destruction was demonstrated, it was not as high as attained in earlier work in HCB. This is attributed to problems with sample introduction in the three-inch reactor, compared to the six-inch reactor used previously.

Limitations of the HTFW Reactor

Two requirements for efficient operation of the HTFW Reactor may be regarded as limitations for degradation of hazardous materials. First, for efficient radiation heating to occur, the sample must possess reasonable optical absorption in the near infrared. If the substance is optically transparent, an auxiliary absorbing material (such as .carbon) must be added. The volatile chlorinated hydrocarbons considered in this program were introduced as vapors with low optical absorption. The transfer of energy to the vapor via fine carbon particles involves collisions between the carbon and vapor molecules which is inherently less efficient and slower than direct optical absorption. In the case of hazardous materials on solids or sediments, the requirement will often be satisfied automatically by the absorption characteristics of the soil or sediment. The other requirement is that the sample be finely divided. While the limiting particle size depends on optical absorption, experience has demonstrated that sample size should usually be -100 mesh or finer. This precludes handling of waste directly in many instances and will often demand preprocessing. On the other hand, many soils and sediments have the required fineness for direct injection, and up to 50 percent water may be tolerated in certain cases.

EXPERIMENTS

Design of Experiments

The experimental program on the thermal destruction of chlorinated hydrocarbons (CLHC) was based on our experience in conducting preliminary studies, the destruction of HCB and PCB, as discussed earlier. All experiments were scheduled to be carried out over consecutive days to ensure that no other materials entered the reactor during the test period.

Statement of Work

As outlined in the proposal, the project was conducted under eight tasks as follows:

Task A: Preparation of a detailed program plan including development of quality assurance methods to guarantee validity of analytical results, and preparation of safety procedures to assure personnel safeguards during the experimental phase of the program.

Task B: Performance of thermal destruction tests on dichloromethane at 2200°C.

Task C: Performance of thermal destruction tests on carbon tetrachloride at 2200°C.

Task D: Performance of thermal destruction tests on Freon-12 at 2200°C.

Task E: Performance of thermal destruction tests on 1,1,1-trichloroethane at 2200°C.

Task F: Performance of thermal destruction tests on hexachlorobenzene at 2200°C, 2000°C, 1700°C, and 1400°C; also, with and without the addition of calcium oxide.

Task G: Correlation and interpretation of all data and incorporation in a final report.

Test Matrices

The test and effluent samples to be collected for a typical CLHC are given in Table 2-2.

Both the soil background and the CLHC samples were run in triplicate to provide additional precision and accuracy. For trichloromethane, three additional tests were performed at successively lower core temperatures (1000°C, 1700°C, and 1400°C) to assess the importance of core temperature.

TABLE 2-2: TYPICAL TEST MATRIX FOR VOLATILE CHLORINATED HYDROCARBONS

TEST NO.	MATERIAL	FEED	PAN	CARTRIDGE	HEAT EXCHANGED
1	Carbon	X	X	X	
2	Carbon + CLHC	X	X	X	
3	Carbon		X	X	
4	Carbon + CLHC		X	X	all at
5	Carbon		X	X	2200°C
6	Carbon + CLHC		X	X	X

For HCB, the above typical matrix was augmented to illustrate the "gettering" of chlorine by lime. In order to demonstrate gettering and production of a nonleaching product, soil was used with HCB. Therefore, the matrix of tests given above was modified by substituting "soil" for "carbon" and including additional tests with lime. The extra tests were:

TEST NO.	MATERIAL	FEED	PAN	CARTRIDGE	HEAT EXCHANGER	BUBBLERS
6	Soil + HCB		X	X		X
7	Soil + Lime	X	X	X		
8	Soil + Lime + HCB	X	X	X	X	X

Bubbler samples were taken at the end of Test 6 document, the chlorine present without the addition of lime; those taken at the end of Test 8 were taken to document the chlorine remaining after "gettering" by lime.

In the earlier plans, the variation in core temperatures was assigned to tests on HCB; however, they were performed in tests on trichloroethane as indicated above. Also, the earlier plans called for measurements in vinyl chloride. Because of unavailability of vinyl chloride, Freon-12 was substituted.

Sample Size

Sample size was chosen to allow determination of destruction of efficiency to 99.9999 percent or better. In a typical experiment, the feedstock consisted of approximately 2kg solids with a loading of 20g CLHCs (1 percent) which was introduced at a rate of approximately 100g/min. for 20 minutes. If all of the effluent was analyzed, 20g of sample had to be detected to realize the desired sensitivity. In the case of vapor samples, approximately 1/12 of the total vapor was sampled, requiring a detection sensitivity of 1.7g. Since detection sensitivities with GC and electron capture are usually at least on order of magnitude better than this, the required sensitivity was realized.

Reactor Modifications

Prior to actual experimentation, the reactor was fitted with a new core to ensure the absence of cross contamination by any previous tests. The entire reactor from just below the hot zone to the final exit to the scrubber (see Figure 2-3) was disassembled and scrubbed with water and detergent. After a water rinse, the stainless steel parts were treated with sulfuric acid and then passivated with dilute nitric acid and finally rinsed again with water.

A gas/liquid injection system was added to allow co-introduction of gas/liquid samples with the solid substrate, as will be described in the next sections.

Feedstock Preparation

All of the feedstocks except HCB are volatile halogenated hydrocarbons, and all of these except Freon-12 are liquids under normal temperature and pressure. Liquid samples are most easily introduced into the reactor by causing them to be absorbed onto a solid (such as fine carbon or clay) at a known concentration, and introducing the spiked solid with a Vibra-Screw Feeder. Because of the volatility of these samples there was a question about the integrity of such samples as they were handled, poured into the hopper, etc., and exposed to air. Therefore, it was decided to introduce the volatile samples as vapors, mixed with the sweep nitrogen. The absorbing fine carbon was introduced separately with the Vibra-Screw Feeder. Hence, all feedstocks except HCB were used as delivered.

Preliminary mixing of HCB and soil was performed in a hood with a high flow rate, thus eliminating any exposure to HCB vapor or soil with HCB. The mixed materials were then placed in clean sealed metal cans and carried to the V-blender. After careful addition to the blender, the sample was blended for a minimum of four hours after which it was again placed into the cans and sealed. During blending and transfer of material, personnel wore disposable gloves, coveralls, and dust masks. Final distribution and weighing into labeled cans was performed under the hood. All exposed surfaces were cleansed with hexane and the rags used were sealed in a can for disposal.

Safety Procedures

The flasks to be used for vapor entrainment were loaded with CLHCs in the laboratory under a hood, using standard laboratory practice.

Safety procedures for mixing HCB and soil have been detailed above under *Feedstock Preparation*.

During the Reactor operation, each crew member had specified tasks. The person responsible for loading samples into the hopper wore not only disposable gloves and coveralls, but a mask designed to trap organic vapors as well as dust. Other crew members wore coveralls, gloves, and dust masks. A plastic tent structure had been erected to protect personnel against potential release of sample material during Reactor loading. Fresh garments were available as needed. Visitors were kept at a distance from the Reactor and were supplied with coveralls, gloves, and masks as needed.

Tests of December 8–13, 1982

Most of the tests were carried out during the period of December 8–11, 1982. On Friday afternoon, December 11, the Reactor became clogged during the second test involving HCB in soil, and tests had to be discontinued. At that time, it was felt that the remaining tests would not be completed prior to dismantling of the Reactor and moving to a new location. However, the Reactor was successfully repaired over the weekend and the last six tests on HCB/soil were carried out.

Feedstock Introduction

Feedstock vapor was introduced directly into the nitrogen sweep gas. The liquid in a gas-washing bottle was maintained at 0°C in an ice bath, and the rate of nitrogen flow bubbling through the bottle was adjusted to vaporize approximately 1 g/min. of feedstock. Assuming that the nitrogen flowrate was low enough to permit the vapor to reach equilibrium, the rate of nitrogen flow at standard temperature and pressure to produce 1 g/min. of feed is given by:

$$F_{N_2} = \frac{760}{VP} \times \frac{22.4}{MW}$$

Where F_{N_2} = desired nitrogen flow, l/min.
VP = vapor pressure of the feed gas at 0°C, mm Hg.
MW = molecular weight of feed gas.

For the three liquid samples the required nitrogen flow rates are estimated in the following table:

	CH_2C1_2	$CC1_4$	CH_3CC1_3
MW	85	154	133
VP @ 0°C (mmHg)	130	33	36
F_{N_2} (1/min.)	1.54	3.35	3.56

These flows were easily realized using standard flow meters. The calculation was only used to produce an approximate sample flow of 1 g/min. The actual feed during a 20-minute test was determined by loss of weight of the gas-washing bottles.

In a typical test the gas-washing bottle containing a halogenated hydrocarbon liquid gas placed in the ice bath until it had equilibrated. Just before the test, it was removed from the bath, dried quickly, and weighed. It was then returned to the bath, attached to the nitrogen line and to the sweep line into the Reactor, and the test was begun. After the test, the bottle was again removed, dried, and weighed again. Between tests, the inlet and outlet were sealed with parafilm to prevent water condensation or contamination.

The procedure with dichlorodifluoromethane (Freon-12) was slightly different because it is a gas at room temperature and pressure. The Freon was contained in a standard 14 oz. pressurized refrigerant can with valve. The can was not cooled and the desired flow rate for 1 g/min. was estimated by:

$$F_{12} = \frac{22.4}{MW} = \frac{22.4}{121} = 0.189 \text{ 1/min.}$$

The actual weight of Freon used during a test was determined by the loss of weight of the container.

For all 4 of the vapor samples discussed above, fine carbon (-100 mesh) was co-introduced into the Reactor via the Vibra-Screw Feeder at the rate of approximately 100 g/min. The HCB-in-carbon sample was introduced in the same fashion.

Effluent Collection

Vapor samples (with entrained fine particulates) were withdrawn continuously from a point in the gas discharge line directly before the cyclone and baghouse, using a calibrated pump. Since the gas flowing through the Reactor is controlled (i.e., the Reactor is a closed system with no leaks), a metered sample flow may be related to total throughput. The vapor samples passed through a water-cooled heat exchanger prior to entering a cartridge where any undegraded CLHCs were adsorbed. For HCB, the cartridge contained a polyurethane plug, as in previous experiments: For the other CLHCs, the cartridge contained activated charcoal, following NIOSH methods for "purgeable halocarbons." Sampling points are indicated in Figure 2-3.

Vapor sampling began *before* introduction of CLHC had begun and was terminated *after* CLHC feed had terminated. (For a nominal 20 g input of CLHC, sampling time was approximately 20 minutes at a rate of 1 g/min.). After a test, the cartridge was removed and refrigerated prior to shipment to an analytical laboratory.

Solids fell into a pan at the bottom of the Reactor. A fresh one-gallon steel can was positioned under a stainless steel funnel to receive the sample automatically. At the termination of a test the can was immediately capped preparatory to shipment to a laboratory for analysis.

The heat exchanger was necessary to ensure that the temperature of the vapor effluent was low enough to be trapped efficiently by the cartridges. Previous work had shown that the material trapped in the heat exchanger was small but not negligible. Therefore, the entire heat exchanger glassware was shipped for analysis; however, the heat exchanger was used over an entire series of tests, so any remanent source material would be apportioned to the various tests according to the inputs.

Effluent Analysis

Two EPA-approved laboratories were selected to perform analyses. WCTS of Cerritos, California, was the primary laboratory, with confirming work performed by the Environmental Monitoring and Services Center (EMSC) of Rockwell International in Newbury Park, California. In the standard matrix of six tests the middle pair of carbon and carbon/CLHC effluent samples was shipped to Rockwell, while the others were analyzed by WCTS.

Analysis of the outside sample pairs by a single analytical laboratory was expected to establish average effluent levels and determine whether tests had proceeded uniformly. Analysis of the

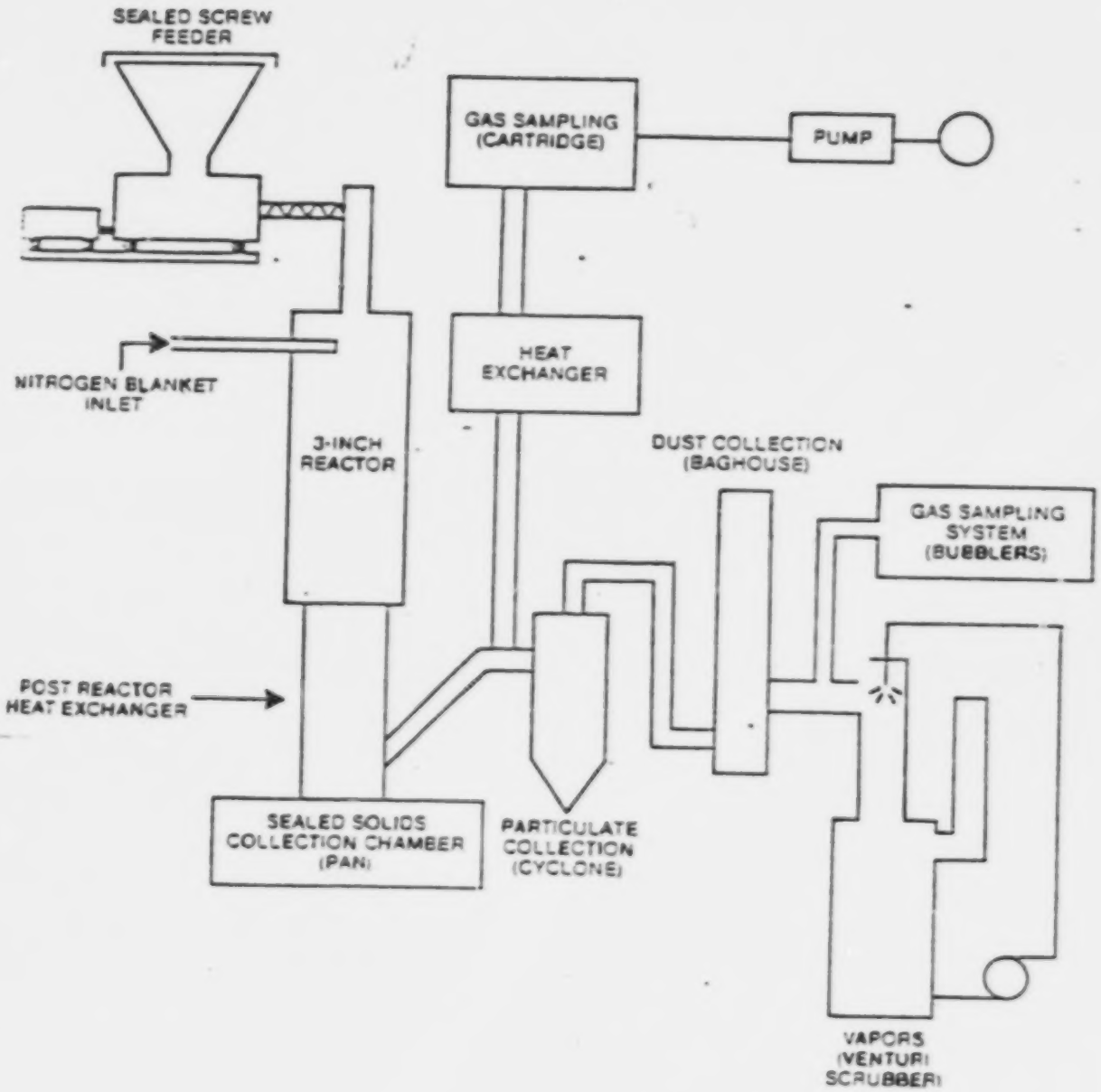


FIGURE 2-3: SCHEMATIC DIAGRAM OF THE HTFW REACTOR SYSTEM

central pair of samples by a second laboratory was expected to be a basic check on the first laboratory using samples expected to be most typical for a set of tests.

Sampling and analysis methodologies were selected with consultation of WCTS to meet the special nature of the effluents (e.g., a vapor with relatively large quantities of fine carbon) and also provide the necessary sensitivity. For HCB the selected sampling and analytical methodology was based on the work of IERL in Research Triangle Park. The adsorbing cartridge contained a polyurethane foam (PUF) plug with a glass filter to trap the fine carbon. Analysis, after extraction of sample from both PUF and pan solids, was essentially that of EPA Method 612 for Chlorinated Hydrocarbons.

For the remaining four vapor samples a new, larger cross section cartridge, containing activated charcoal and a glass filter for carbon was designed, based on NIOSH Method P&CAM127 for Organic Solvents in Air. After extraction with selected solvents, analysis was essentially that of EPA Method 601 for Purgeable Halocarbons.

All analysis involved solvent extraction followed by GC with electron capture detection. The methodology involved solvent extraction followed by GC with electron capture detection. The methodology is summarized in the following table:

Sample	Extraction Solvent	GC Column Temperature	Related EPA Method
1. Methylene Chloride	Iso octane	60°C	601
2. Carbon Tetrachloride	Iso octane	120°C	601
3. 1,1,1-Trichloroethane	Iso octane	120°C	601
4. Freon-12	Pentane	50°C	601
5. Hexachlorobenzene	Ether/hexane	160°C	612

Charcoal Cartridges

For analysis, the activated charcoal was poured into a 7 cm x 45 cm column and desorbed with 250 ml of solvent. The entire column was shaken continuously for 3 to 5 minutes. The eluant was collected and analyzed immediately for the compound of interest by direct injection into the GC.

The eluant was concentrated and brought to 10 ml for analysis of nonvolatile chlorinated hydrocarbons. The extracts were analyzed on a gas chromatograph equipped with an electron capture detector.

The gas chromatograph conditions for the chlorinated solvents were as follows:

Gas Chromatograph:	Varian 3700
Column:	6' x 2mm glass column packed with 1% SP–1000 on Carbonpack B
Detector:	Electron Capture
Detector Temperature:	300°C
Injector Temperature:	200°C
Column Temperature:	See Table
Extraction Solvent:	See Table

PUF Cartridges

The PUF filter samples were extracted in a Soxhlet extractor which had been precleaned by extracting continously with 10 percent ether in hexane for 20 hours. The ash on the screen, the glass filter, and the PUF filter were placed in the extractor and the sample was extracted continuously with 10 percent ether in hexane for 24 hours. The extract was concentrated, brought to 10 ml and analyzed by direct injection into the GC. The gas chromatographic conditions were as follows:

Gas Chromatograph:	Varian 3700
Column:	6' x 2mm glass column packed with 1.95% SP–2401 and 1.56 SP–2250 on 150/120 mesh Supelcoport
Detector:	Electron Caputre
Detector Temperature:	300°C
Injector Temperature:	250°C
Column Temperature:	160°C

Pan Samples

The pan samples were approximately 2000 grams each. The sample size made it necessary to use a method of extraction that would include agitation of the sample. Also, the sample size was much too large for extraction in a normal size laboratory soxhlet extractor.

Each sample was divided into three aliquots. Each aliquot was placed into a two-liter Erlenmeyer flask. A sufficient amount of methylene chloride was added to each sample aliquot to achieve saturation. An additional 300 milliliters was then added to the first flask, and the flask was agitated for approximately ten minutes.

The excess methylene chloride from the first flask was decanted into the second flask, and the second flask was agitated for approximately ten minutes. The excess methylene chloride was decanted into the third flask, the third flask was agitated for approximately ten minutes. The excess methylene chloride from the third flask was decanted into a Kuderna-Danish apparatus, and the methylene chloride was evaporated.

This process was repeated one more time.

The final step was to add 300 ml of fresh methylene chloride to each two-liter flask, and agitate each flask for 10 minutes. The excess methylene chloride was decanted into the Kuderna-Danish apparatus, and the methylene chloride in each flask was removed by filtration through a Buchner funnel. The total pan ash of each sample was recovered from the filtration step and stored.

All methylene chloride fractions from each extraction step were collected and concentrated in the same Kuderna-Danish apparatus.

The total extract volume was reduced to less than 1.0ml, exchanged into hexane, and brought to 1.0ml for analysis.

The extract was analyzed by direct injection into the GC. The analysis conditions were as follows:

Gas Chromatograph:	Varian 3700
Column:	6' x 2 mm glass column packed with 1.95% SP–2401 and 1.56% SP–2250 on 100/120 mesh Supelcoport.
Detector:	Electron Capture

Detector Temperature: 280°C

Injector Temperature: 250°C

Column Temperature: 180°C

Miscellaneous Samples

The heat of exchanger samples were extracted using the same procedure as the PUF filter samples. The soil feedstock was extracted in parallel with the pan ash samples. The analysis conditions for the heat exchange samples were identical to the above described conditions for the pan samples.

The analytical methodology described above was used by WCTS, the principal analytical laboratory. Rockwell's methods were similar.

While analysis was principally for the specific hazardous material placed in the feedstock, the GC traces were examined for evidences of other materials which might be products of incomplete pyrolysis, with special attention given to either tetrachlorodibenzodioxin or tetrachlorodibenzofuran.

No evidence was seen of these last two compounds in this particular test series.

SECTION 3

AIR RESOURCES BOARD'S (ARB) EVALUATION TO DETERMINE EMISSIONS FROM SUNOHIO'S MOBILE PCB TREATMENT PROCESS

Three evaluation tests were conducted to allow determination of emissions from SUNOHIO's mobile PCB treatment process. The mobile unit was tested while treating contaminated oils at three locations: Chevron's USA refinery at El Segundo, California; Pacific Gas and Electric (PG&E) Company's facility at Union City, California; and Maxwell Laboratory's facility in San Diego, California.

PCBs were not detected in samples of emissions taken at two of the tests. However, relatively high benzene and aliphatic hydrocarbon concentrations were measured in the units' uncontrolled exhaust gases. Measured concentrations ranged from 18 to 7,000 ppm for benzene and 700 to 2,700 ppm for aliphatic hydrocarbons. Low process volumetric flow rates resulted in the mass emission rates for benzene and the aliphatic hydrocarbons to values of approximately 0.1 lb/hr. and below. Data from samples taken by the South Coast Air Quality Management District (SCAQMD) staff during the El Segundo test indicate that dioxins and furans are not present above the limit of detectability.

The efficiency of the carbon adsorption control system for preventing emissions to the atmosphere of benzene and aliphatic hydrocarbons was found to have varied from approximately 99 to 30 percent, indicative that carbon adsorption breakthrough occurred. The 30 percent efficiency calculation was based upon concentration measurements from the evaluation test conducted at the PG&E facility.

An alternative control system was tested that utilized an oil fired furnace, a component of the PCBX process, to incinerate the emissions. Furnace exhaust gas samples indicate a general reduction in concentration of compounds measured across the furnace. Benzene and toluene were not detected in the furnace exhaust gas.

INTRODUCTION

On December 2 and 10, 1982 and November 30, 1983, the ARB's Engineering Evaluation Branch conducted evaluation tests on chemical processing equipment designed to reclaim transformer oils contaminated with PCBs. The process tested is known as the "PCBX" process and was developed by SUNOHIO, a partnership between the Sun Company of Radnor, Pennsylvania and the

Ohio Transformer Corporation of Louisville, Ohio. The equipment is installed on two mobile trailers and can be driven to different geographical localities to treat contaminated oils on site. The first test was conducted on December 2, 1982 at Chevron's USA El Segundo refinery. This was a joint venture between SCAQMD and the ARB. The second test was conducted on December 10, 1982 at a PG&E facility in Union City. The third test was conducted on November 30, 1983 at the San Diego facility of Maxwell Laboratory.

The objectives of the evaluation tests were to allow determination of emissions from the unit's vacuum degasser and determination of the efficiency of two prototype emission control systems. One control system consists of an oil mist eliminator in combination with an activated charcoal filter to control emissions from the vacuum degasser's vent pipe. The other control system utilizes an oil fired furnace that is a component of the PCBX process to incinerate the emissions.

CONCLUSIONS AND RECOMMENDATIONS

Based on the analytical results and staff experience obtained from the ARB's evaluation test conducted on the SUNOHIO PCBX process, the following observations are made:

1. The activated carbon adsorption canister used during testing is not big enough to provide effective emissions control for an extended period of time, the control system should be (1) redesigned to have a larger activated carbon adsorption unit, or (2) revise the maintenance schedule for the present carbon canister to require canister replacement with a frequency commensurate with a demonstrated breakthrough time.

2. If emissions are to be prevented from the carbon canister, the carbon canister breakthrough should be monitored with a continuous analyzer.

3. Based upon the results of this test, the oil fired furnace as a control device appears to be effective.

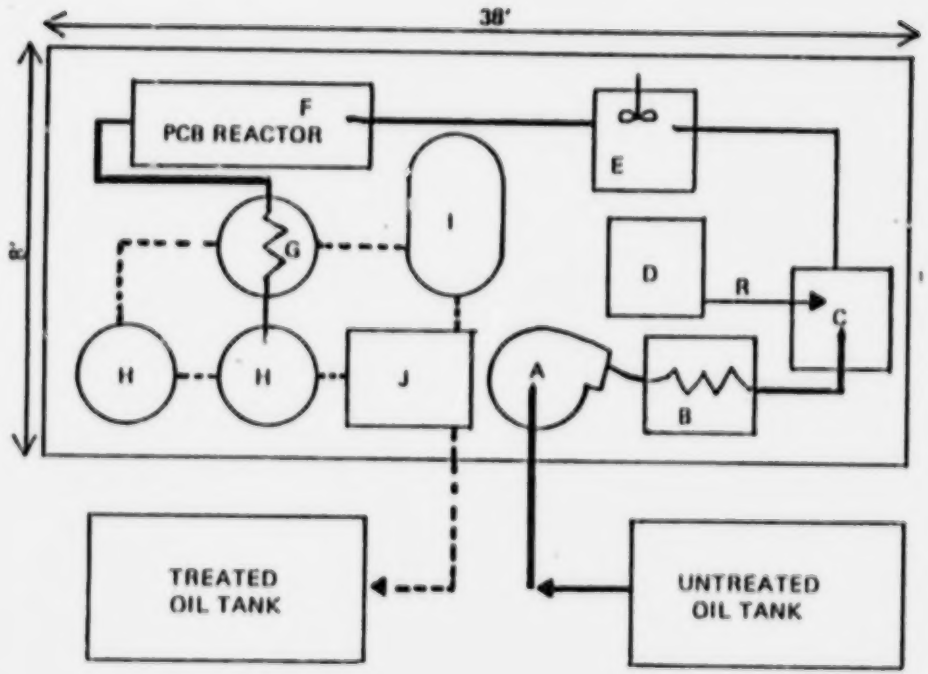
EXPERIMENTAL PROCEDURES

Process Description

SUNOHIO's PCBX process is a chemical treatment process designed to strip chlorine atoms from the PCB compound to form sodium chloride. The resulting biphenyl is polymerized into polyphenylene. A process schematic is presented in Figure 3-1.

FIGURE 3-1

SUNOHIO Process Schematic



WHERE:

A – ADJUSTABLE RATE, POSITIVE DISPLACEMENT PUMPS

B – AN AUTOMATICALLY CONTROLLED HEATER

C – A METERED FLOW REAGENT INJECTION DEVICE

D – REAGENT STORAGE

E – A MOTOR ACTUATED MIXING CHAMBER

F – A SPECIALLY DESIGNED REACTION VESSEL

G – A SERIES OF HEAT EXCHANGERS

H – DUAL FILTER BEDS

I – A VACUUM DEGASSER

J – A 1,000 GALLON RETENTION TANK

PCB-contaminated oils are pumped from either a storage tank or an energized transformer to an automatically controlled heater at flow rates ranging from 500 to 900 gallons per hour. Initial PCB concentrations in the untreated oil are reported to be as high as 10,000 ppm. Process temperatures are maintained below 302°F (150°C) at an average operating pressure of 40 psi. Reagent is injected into the oil downstream of the heater. A mixing chamber is used to ensure complete blending between the reagent and oil. The residence time required for reaction to occur is provided by passing the mix through an extended length of tubing located between the mixing chamber and heat exchangers. Solids are removed from the treated oil by a centrifuge (not shown in schematic) and gases by a vacuum degasser. Both the centrifuge and vacuum degasser are process equipment from which emissions to atmosphere can occur. The contaminated oil is continuously recirculated and reagent injected until PCB concentrations in the oil are reduced to approximately 2 ppm.

Exhaust gases from the vacuum degasser and centrifuge are vented through two 2-inch diameter pipes directed out the side of each trailer. The vacuum degasser is in the main trailer and the centrifuge in the auxiliary trailer. There is a vent pipe for each of the process units.

Description of the Two Proposed Emission Control Systems

Two emission control systems, designed by SUNOHIO, were proposed for testing. One system consists of condensate knockout drums arranged in series with a carbon cartridge. The other proposed system utilizes the on-board PCBX process furnace to combust emissions.

The principle components of the knockout drum/carbon cartridge emission control device are two 55-gallon drums arranged in series with an oil mist eliminator/activated charcoal filter unit attached to the outlet of the last drum. Also, a condensate knockout is placed in between the drums. This system is intended to be attached directly to the vacuum degasser and centrifuge vent pipes to control emissions before being discharged to the atmosphere. Each process unit will have a control system dedicated to it.

The proposed combustion control system was connected to the vacuum degasser's vent pipe. A vacuum pump draws vapors from the degasser and discharges them into a 30-gallon pressure vessel for storage. The PCBX process furnace fires intermittently. When the burner is on, a furnace activated solenoid valve opens and vapors are drawn from the pressure vessel to the furnace. When the burner is idle, the solenoid valve is closed. As a safety measure when the furnace is off, if the system's pressure exceeds a pre-set value, a pressure relief valve opens and vapors are vented to the atmosphere through an activated carbon cannister.

Test Methods

1. SUNOHIO Evaluation Test Conducted at Chevron's USA El Segundo Refinery

The ARB staff conducted tests to evaluate uncontrolled emissions from the vacuum degasser while the SUNOHIO unit was treating PCB-contaminated oil directly out of a transformer. Samples representing uncontrolled emissions were taken from the vent hose at the inlet to the emission control system. The types of samples taken and the methods of sampling are summarized in Table 3-1, Summary of Sampling Methods. Organic compounds were collected on Tenax resin, florisil and in bags and analyzed by GC/MS, GC/FID, and GC/ECD.

The ARB staff did not sample emissions across the activated charcoal filter. Per discussions held at a pre-test meeting, the participants agreed that the SCAQMD staff would sample at these points to obtain information they would require for their permitting process.

Low molecular weight hydrocarbons were sampled using two sampling trains: a Tenax tube was placed after a cold trap in the series arrangement. A total of 7 liters of exhaust gases were sampled at a rate of 0.2 liters per minute. The adsorbed gases were thermally desorbed and analyzed by GC/FID and GC/ECD. For the bag sampling, three-bag samples were analyzed using GC/FID and GC/MS. A 27-minute sample was collected in the first bag at a rate of 0.8 liters per minute. Simultaneous samples for 15 minutes at 0.8 liters per minute were drawn into the last two bags.

Two samples for the PCB analysis were collected on florisil adsorbent. A total of 8.92 liters were sampled through one of the florisil tubes at a rate of 0.12 liters per minute and 5.27 liters through the other at 0.1 liters per minute. A florisil blank was taken before the start of the first PCB, florisil test run.

Two ambient samples for background analysis were taken in bags, but without the probe and impinger/ice bath. One bag sample was given to SCAQMD and the other to the ARB's Haagen-Smit Laboratory for analysis.

The results of all laboratory analyses are discussed in Result and Discussion, Summary and Discussion of Test Results, and presented in Table 3-2.

SCAQMD conducted emission tests concurrently with the ARB's evaluation test. SCAQMD tested to determine the efficiency of the carbon canister and the emissions to atmosphere from the control system. The sampling locations were primarily used in testing the effectiveness of the emission control system's carbon canister for both the vacuum degasser and the centrifuge. A summary of the SCAQMD test results is presented in Table 3-3.

Flow rates were measured by the SCAQMD test team using a Roots meter attached to the outlet of the carbon canister. These flow rates were used by the ARB in calculating pollutant mass rates.

Additionally, Chevron USA contracted TRW Inc. to perform tests concurrent with the ARB and SCAQMD for audit purposes. Results of analyses done by TRW on samples of the vacuum degasser effluents are summarized in Table 3-4.

2. **SUNOHIO Evaluation Test Conducted at a PG&E Facility in Union City**

In addition to testing the uncontrolled emissions from the vacuum degasser, tests to allow determination of emissions to atmosphere after the control system were also conducted. At the request of the ARB, SUNOHIO did not replace the activated carbon canister used at El Segundo. The control system's configuration for the Union City test was identical to that used during testing in El Segundo. However, the mobile unit rather than being used to treat the oil directly out of a transformer, as was done for Chevron USA at El Segundo, the mobile unit treated PCB-contaminated oil taken from a storage tank.

The test methods and strategy used at the PG&E facility were the same as those applied at El Segundo and are summarized in Table 3-1. Results of the test are presented in Table 3-2.

Flow rates were measured by the ARB test personnel using a Roots meter attached to the outlet of the carbon cannister.

The Bay Area Air Quality Management District (BAAQMD) observed the ARB evaluation test and took grab samples of the exhaust gases being vented to the atmosphere. The BAAQMD Summary of Results is presented in Table 3-5.

3. SUNOHIO PCBX Evaluation Test Conducted at Maxwell Laboratory's San Diego Facility

The previous two tests addressed the effectiveness of the emission control device consisting of two 55-gallon drums arranged in series with an oil mist eliminator and an activated charcoal canister. For the San Diego test, SUNOHIO modified the configuration by eliminating one of the drums and the oil mist eliminator. Samples of uncontrolled and controlled emissions across the system were taken during the test. In addition to the condenser/carbon control system, a combustion control system was also tested.

The condenser/carbon and combustion systems were plumbed off of the vacuum degasser's vent pipe with a "tee" valve. To divert the vapors from one control system to the other merely required the turning of the valve.

The San Diego test strategy remained-the same as that applied to the previous tests. However, the test methods differed slightly. Carbon, rather than Tenax, was used as the adsorbent media to collect hydrocarbons. Combustion gases generated by the PCBX oil furnace were analyzed by continuous monitors for 0_2, CO_2, CO, THC, NO_x, and SO_2 in addition to being samples with carbon tubes and bags. Florisil samples were not taken because PCB was not detected in the vent gas at the other two tests. A summary of results is presented in Table 3-6.

Flow rates from the condenser/carbon control system were measured with a Roots meter. Flow rates from the furnace exhaust duct were calculated from fuel oil analytical data.

Results and Discussion

1. Results From the Test Conducted at Chevron's USA El Segundo Refinery

Results of analyses performed on samples taken from the PCBX process during the ARB evaluation test conducted at Chevron's USA El Segundo refinery are summarized in Table 3-2. Benzene and C_8-C_{12} hydrocarbons were the predominant components measured in the gases vented directly out of the vacuum degasser during the treatment of transformer oil. Benzene concentrations ranged from 400 ppm to 7,000 ppm and hydrocarbon concentrations from 7 ppm to 1,600 ppm. TRW's analytical results for samples taken at the same location as the ARB, Table 3-4, show benzene concentrations exceeding 5,000 ppm and C_5 hydrocarbon concentrations as being 1,400 ppm. TRW results for benzene are in the range of concentrations determined by the ARB and the hydrocarbon concentrations, while not directly comparable to the ARB results, are probably not inconsistent. SCAQMD did not take samples from the vacuum degasser outlet.

PCBs were not detected above the detection limit of the analytical method for any of the ARB samples taken. TRW also sampled for and could not detect PCBs above the limit of detection for their analytical method (1 ppm).

As discussed previously, SCAQMD took samples before and after the activated carbon adsorber and analyzed those samples for PCBs, furans, and dioxins. A summary of test results is presented in Table 3-3. Because they sampled at a different location and the emphasis of their analytical work was different, no direct comparison can be made between the SCAQMD and ARB test results. Test results indicate that furans and dioxins are not present above the detectable limits, less than 4–30 parts per trillion. However, in two samples taken from the centrifuge vent at the inlet and outlet of the carbon cannister, detectable amounts of PCBs were measured; 1.7 (10^{-3}) ppm at the inlet and 8.7 (10^{-6}) ppm at the outlet.

2. **Results From the Test Conducted at PG&E's Union City Facility**

Benzene and aliphatic hydrocarbons were the major components measured in the ARB samples taken from the degasser vent during the treatment of PCB-contaminated oils stored in a tank at a PG&E facility located in Union City. Referring to Table 3-2, the range of concentrations determined for benzene and C_6-C_{12} hydrocarbons was 50 to 950 ppm and 1,900 to 2,700 ppm, respectively.

Benzene and aliphatic hydrocarbons were also the significant components in the treated vacuum degasser vent gas as sampled at the outlet from the control system's activated charcoal adsorber. The range of benzene concentrations was 600-700 ppm and the range of C_6-C_{12} hydrocarbons was 1,400 to 1,600 ppm. BAAQMD also took samples at the charcoal adsorber outlet and test results, presented in Table 3-5, showed: a comparable benzene concentration of 840 ppm (average); a comparable D_c-C_{12} hydrocarbon concentration of 1,500 ppm; and total organic and nonmethane organic compound concentrations of 2,600 ppm (average) and 2,400 ppm (average), respectively.

The control system's charcoal canister was the same one used at the El Segundo test. Results of a comparison between the concentrations determined for the inlet and outlet of the control system are indicative of carbon adsorption breakthrough. The reduction of both benzene and aliphatic hydrocarbons was approximately 30 percent across the control system.

PCBs were not detected above the detection limit of the analytical method for any of the ARB samples taken. BAAQMD did not analyze their samples for PCB.

TABLE 3-1

SUMMARY OF SAMPLING METHODS

PARAMETER TO BE MEASURED	SAMPLING METHOD	ANALYTICAL METHOD
Hydrocarbons	Tenax	GC/ECD
		GC/FID
	Bag	GC/FID
		GC/MS
PCB	Florisil	GC/ECD
PCB in oil to be treated	Liquid Grab	GC/ECD
Ambient Air	Bag	GC/FID
		GC/MS
Flow Rate	Roots Meter	Not Applicable

TABLE 3-2

SUMMARY OF ARB TEST RESULTS
(Chevron USA, El Segundo, & PG&E, Union City)

FACILITY	SAMPLING LOCATION	ANALYTICAL METHOD	SAMPLING METHOD	COMPOUND DETECTED	CONCENTRATION (ppm)
Chevron USA, El Segundo Refinery	Inlet to the Control System	GC/MS; GC/FID; GC/ECD	Tenax	Benzene	400
				Other Aromatics	10
				$C_8 - C_{12}$ hydrocarbons	1,100
			Bag[4]	Trichlorobenzene	trace, not determined
				Benzene	7,000
				Other Aromatics	90
				$C_8 - C_{12}$ hydrocarbons	1,800
				Trichlorobenzene	trace, not determined
			Bag[4]	Benzene	350
				Other Aromatics	3
				$C_8 - C_{12}$ hydrocarbons	700
				Trichlorobenzene	trace, not determined
			Florisil[3]	PCB	N.D.[1]
			Florisil[3]	PCB	N.D.[2]
	PCBX Oil Treatment Line	GC/ECD	Grab	PCB in untreated oil	1,330 ppm(w/w)
				PCB in treated oil, end of ARB's test[5]	1,030 ppm(w/w)
	Ambient Air	GC/MS; GC/FID; GC/EC	Bag	Benzene	no detectable compounds under identical analytical conditions
				Other Aromatics	
				$C_8 - C_{12}$ hydrocarbons	
				Trichlorobenzene	
PG&E, Union City	Inlet to the Control System	GC/MS; GC/FID	Bag	Benzene	50
				Other Aromatics	4
				Alcohols	2
				$C_8 - C_{12}$ hydrocarbons	2,700
			Bag	Benzene	950
				Other Aromatics	20
				Alcohols	10
				$C_8 - C_{12}$ hydrocarbons	1,900
		GC/ECD	Florisil[3]	PCB	N.D.[2]
	Outlet from the Control System	GC/MS; GC/FID	Bag	Benzene	600
				Other Aromatics	30
				Alcohols	60
				$C_8 - C_{12}$ hydrocarbons	1,400
			Bag	Benzene	700
				Other Aromatics	20
				Alcohols	10
				$C_8 - C_{12}$ hydrocarbons	1,900
		GC/ECD	Florisil[3]	PCB	N.D.[2]
	Ambient Air	GC/MS; GC/FID	Bag	Benzene Other Aromatics Alcohols $C_8 - C_{12}$ hydrocarbons	no compounds were detected under identical analytical conditions
	PCBX Oil Treatment Line	GC/ECD	Grab	PCB in untreated oil	188 ppm(w/w)
				PCB in treated oil, end of ARB's test[5]	482ppm(w/w)

1 N.D. = Not detected. Limit of detection with respect to volume sampled; 10 $\mu g/m^3$.
2 N.D. = Not detected. Limit of detection with respect to volume sampled; 20 $\mu g/m^3$.
3 Detection limit of the analytical method; 0.002 $\mu g/m^3$.
4 Samples taken simultaneously.
5 The conclusion of the ARB evaluation test did not correspond to the completion of the oil treatment process.

TABLE 3-3

SUMMARY OF SCAQMD TEST RESULTS
(Chevron USA, El Segundo Refinery)

Sampling Location	Sampling Method	Analytical Method	Compound	Concentrations Across The Activated Carbon Adsorber (ppm)	
				Inlet	Outlet
Centrifuge Vent	Ethylene Glycol in an impinger train	GC/EC; GC/MS	Polychlorobiphenyl	0.0017	$8.66(10^{-6})$
			Furans[1]	<0.0000357	$<8.33(10^{-6})$
			Dioxins[1]	<0.0000342	$<7.99(10^{-6})$
Vacuum Degasser Vent	Ethylene Glycol in an impinger train	GC/EC; GC/MS	Polychlorobiphenyl[1]	$<3.92(10^{-6})$	$<3.64(10^{-6})$
			Furans[1]	$<3.77(10^{-6})$	$<3.50(10^{-6})$
			Dioxins[1]	$<3.62(10^{-6})$	$<3.36(10^{-6})$
Ambient Air	Bag	GC/EC; GC/MS	Vinylchloride	<0.01	

[1] Below limit of detectability

TABLE 3-4

SUMMARY OF TRW INCORPORATED TEST RESULTS
(Chevron USA, El Segundo Refinery)

SAMPLING LOCATION	SAMPLING METHOD	NUMBER OF SAMPLES	ANALYTICAL METHODS	COMPOUND DETECTED	CONCENTRATION (PPM)
Inlet to the Control System	Bag[1]	1	GC/MS	Methane	74
				Ethane	22
				C_3 Hydrocarbons	52
				C_4 Hydrocarbons	77
				C_5 Hydrocarbons	1,400
	Tenax[1]	2	GC/MS	Benzene	<5,000[a]
	Florisil[1]	1	GC/MS	Benzene	<5,000[a]

[1] Tenax, bag, and Florisil samples were analyzed for a number of compounds including chlorinated dibenzofurans, chlorinated biphenyls, chlorinated naphthalenes and chlorinated dibenzodioxins which were not detected above the detection limit of 1 ppm. Benzene was the only compound found in the tenax and florisil samples.

[a] Above limit of detection.

TABLE 3-5

SUMMARY OF BAAQMD TEST RESULTS
(PG&E, Union City)

SAMPLING LOCATION	SAMPLING METHOD	COMPOUNDS OR CLASS OF COMPOUNDS	CONCENTRATIONS (PPM)		
			Run A	Run B	Average
Outlet of Control Device	Evacuated Cylinder with Silica Gel	Total Organic Carbon	2,768	2,473	2,621
		Nonmethane Organic Carbon	2,605	2,303	2,454
		Benzene	938	743	841

3. Results From the Test Conducted at the Maxwell Laboratory in San Diego

A summary of test results for the ARB evaluation test conducted in San Diego is presented in Table 3-6. Emissions were measured during two distinct phases of the PCBX process: (i) degassing and (ii) dechlorination. Concentration values in Table VII footnoted with a (1) were measured during the degassing phase and those footnoted with a (2) were measured during the dechlorination phase.

Benzene concentrations in the uncontrolled vacuum degasser emissions, measured at the common inlet to both control systems, ranged from 18 ppm to 220 ppm. Toluene was also measured at concentrations ranging from 0.1 ppm to 290 ppm. Concentration values preceeded by a less than sign (<) implies that the corresponding compound was below the limit of detectability.

At the outlet from the condenser/carbon control systems, measured benzene concentrations ranged from 10 ppm to 23 ppm and toluene from 0.1 ppm to 26 ppm. Benzene and toluene were not measured above the 0.1 ppm limit of detection in the exhaust gases from the combustion control device.

Products of combustion in the furnace exhaust gas were monitored when the furnace was fired on fuel oil only and when it was fired with a mixture of fuel oil and vacuum degasser vapors. When combusting fuel oil only, the following compounds were measured: 75 ppm SO_2, 72 ppm NOx, 9.3 ppm THC, 133 ppm CO, 10.2 percent CO_2 and 9.7 percent O_2. When vacuum degasser vapors were added for combustion in the furnace, measured concentrations were: 78 ppm SO_2, 92 ppm NOx, 24 ppm THC, 200 ppm CO, 10.2 percent CO_2, 9.1 percent O_2, 0.1 ppm benzene and 0.1 ppm toluene.

Samples taken before and after the control devices were speciated to determine the types of compounds present in the emissions. The results are tabulated in Table 3-7. For comparison purposes, a sample of ambient air was taken. The compounds detected in the ambient sample were all at the part per billion (ppb) level. The magnitude of the other concentration values measured in the uncontrolled and controlled emissions were at the part per million level. Columns 2, 3, and 6 present the results of speciating the samples of the uncontrolled emissions from the vacuum degasser and column 4, 5, and 7, the controlled emissions.

TABLE 3-6

SUMMARY OF ARB TEST RESULTS
(Maxwell Laboratory, San Diego)

FACILITY	SAMPLING LOCATION	ANALYTICAL METHOD	SAMPLE COLLECTION MEDIA	COMPOUND DETECTED	CONCENTRATION (PPM)
Maxwell Laboratory San Diego	Inlet to Control Systems	GC	Carbon	Benzene	18[a]
					31[b]
					220[b]
				Toluene	<0.1[a]
					90[b]
					290[b]
		GC	Bag	Benzene	50[b]
	Outlet from Condenser/Carbon Control System	GC	Carbon	Benzene	10[a]
					15[a]
					22[b]
				Toluene	<0.1[a]
					<0.1[a]
					26[b]
		GC	Bag	Benzene	20[b]
	Outlet from Combustion System	GC	Carbon	Benzene	<0.1[b]
				Toluene	<0.1[b]
		U.V.	Continuous Analyzer	SO_2	75.3[c]
		Chemiluminescence	"	NO_x	72[c]
		FID	"	THC	9.3[c]
		NDIR	"	CO	133.3[c]
		NDIR	"	CO_2	10.2%[c]
		Paramagnetic	"	O_2	9.7%[c]
		U.V.	"	SO_2	78[d]
		Chemiluminescence	"	NO_x	92[d]
		FID	"	THC	24[d]
		NDIR	"	CO	200[d]
		NDIR	"	CO_2	10.2%[d]
		Paramagnetic	"	O_2	9.1%[d]
	F-Tank	GC/EC	Grab	PCB	68.3 µg/g
	Lazer Tank	GC/EC	Grab	PCB	64.3 µg/g
	PCB in Treated oil, end of ARB Test*	GC/EC	Grab	PCB	3.3 µg/g

[a] PCBx process in degassing mode when this sample collected.
[b] PCBx process in dichlorination mode when this sample collected.
[c] PCBx process oil furnace combusting fuel oil only.
[d] PCBx process oil furnace combusting a mixture of fuel oil and vacuum degasser vapors.

* The conclusion of the ARB evaluation test did not correspond to the completion of the oil treatment process.

TABLE 3-7

Quantitative Analysis of Compounds Present in the Gas Stream Entering and Leaving the Activated Carbon Cannister and Oil Burner

Compound Name	1 Ambient Sample PPBV	2 Carbon Cannister Inlet During Degassing Mode PPMV	3 Carbon Cannister Inlet During Dechlor. Mode PPMV	4 Carbon Cannister Outlet During Dechlor. Mode PPMV	5 Carbon Cannister Outlet During Dechlor. Mode PPMV	6 Burner Inlet During Dechlor. Mode PPMV	7 Burner Outlet During Dechlor. Mode PPMV
1. Chloroethylene (Vinyl Chloride)	<1.0E+00	<1E+00	<1E+00	<1E+00		<1E+00	<1E+00
2. Chloromethane (Methyl Chloride)	<2.0E+00	<2E+00	<2E+00	<2E+00	<1E+00	<2E+00	<2E-01
3. Bromomethane (Methyl Bromide)	<2.0E-01	<2E-01	<2E-01	<2E-01	<2E-02	<2E-01	<2E-02
4. Dichlorofluoromethane (Freon 12)	6.7E-01	3E-02	3E-02	3E-02	6E-01•	6E-02	2E-01
5. Dichloromethane (Methylene Chloride)	6.9E-01	2E+00	3E+00	<3E-01	1E+00	<3E-01	3E-01
6. Trichlorofluoromethane (Freon 11)	3.9E-01	4E+00	6E-01	4E-01	5E-01	4E-01	3E-03
7. 1, 1–Dichloroethylene (Vinylidene Chloride)	<1.0E-01	<1E-01	<1E-01	<1E-01	<1E-02	<1E-01	<1E-02
8. trans–1, 2–Dichloroethylene	<1.0E+00	<1E+00	<1E+00	<1E+00	<1E-01	<1E+00	<1E-01
9. Trichloromethane (Chloroform)	<2.0E-02	<2E+01	9E-02	5E-02	4E-03	1E-01	<1E-03
10. Trichlorotrifluoroethane (Freon 113)	9.6E-01	2E+00	4E-01	4E-01	4E-02	4E-01	2E-01
11. 1,2–Dichloroethane (Ethylene Chloride)	<1.0E-01	<1E-01	<1E-01	<1E-01	<1E-02	<1E-01	<1E-02
12. 1, 1, 1–Trichloroethane (Methyl Chloroform)	6.5E+00	>1E+00	>1E+00	>1E+00	2E-01	>1E+00	4E-02
13. Tetrachloromethane (Carbon Tetrachloride)	4.2E-02	2E-02	<1E-02	<1E-02	<1E-03	1E-02	<1E-03
14. Bromodichloromethane	<1.0E-02	<1E+01	<1E-02	<1E-02	<1E-03	<1E-02	<1E-03
15. 1, 2–Dichloropropane	<2.0E-01	<7E+01	<2E-01	<2E-01	<2E-01	<2E-01	<2E-02
16. Trichloroethylene (TCE)	4.7E-02	9E-01	4E-01	2E-01	2E-02	4E-01	3E-02
17. Chlorodibromomethane	<1.0E-02	<1E+01	<1E-02	<1E-02	<1E-03	<1E-02	<1E-03
18. 1, 2 Dibromoethane (Ethylene Bromide)	<1.0E-02	<1E+01	<1E-02	<1E-02	<1E-03	<1E-02	<1E-03
19. Tribromomethane (Bromoform)	<1.0E-02	<1E+01	<1E-02	<1E-02	<1E-03	<1E-02	<1E-03
20. Tetrachloroethylene (PERC)	1.9E-01	>1E+00	>1E+00	>1E+00	1E-01	>1E+00	6E-02
21. Benzene	3.6E+00		5E+01	2E+01			

Note: 1. Less than symbol (<) preceding a concentration value = below the limit of detection.
2. Greater than symbol (>) preceding a concentration value = minimum value.

4. Discussion of Results

During the El Segundo test, sample was drawn from the inlet to the vacuum degasser's control system and introduced simultaneously into two sample bags. However, laboratory results indicate that one of the bags may have leaked, introducing unwanted dilution air into the sample via the bag material itself or between connectors. The samples in question are identified in Table 3-2 by a "d" footnote: "BAG[d]." Analytical results are tabulated in Table 3-8. Comparing these results, a 95 percent difference in benzene concentrations and a 96 percent difference in the "other aromatics" concentrations were observed between the two samples. A similar comparison between aliphatic hydrocarbons indicates a 56 percent difference. This anomaly points strongly towards the supposition that dilution air leaked into one of the sampling bags. Therefore, the sample bag having lower concentration values will be reported but not factored into the ARB's evaluation process.

Benzene, "other aromatics," and aliphatic hydrocarbon concentrations measured in the vacuum degasser vent gas versus process lapse time are plotted for each test. This measurement site represents the uncontrolled emissions from the vacuum degasser. Figure 3-2 is a plot of the El Segundo test data, Figure 3-3 the Union City test data, and Figure 3-4 the San Diego test data. In all figures, benzene concentrations appear to increase as the treatment of PCB contaminated oil proceeds to completion. This dependence appears strongest for the treatment process conducted at El Segundo than at Union City and significantly less so at the San Diego test. Although lower in magnitude, the same trend was observed for the concentrations of "other aromatics" in the vacuum degasser's vent gas. The dependence on processing time was not evident for the aliphatic hydrocarbons. A gradual growth of aliphatic hydrocarbon concentrations with time was observed at the El Segundo test while a decay was evident for the Union City test. Concentration data for "other aromatics" in the vacuum degasser's vent gas. The dependence on processing time was not evident for the aliphatic hydrocarbons. A gradual growth of aliphatic hydrocarbon concentrations with time was observed at the El Segundo test while a decay was evident for the Union City test. Concentration data for "other aromatics" and aliphatic hydrocarbon were not available from the San Diego test.

The cause behind the observed growth of benzene and "other aromatics" concentrations is merely speculative at this time, per telephone conversations with SUNOHIO personnel. Subsequent measurements and observations made while treating oils in other states lead them to believe that this phenomena may be dependent upon the type of oil being treated rather than inherent with the PCBX process itself.[4] Resolving the cause of the concentration growth would be of interest in future evaluation studies.

TABLE 3-8

Concentration of Benzene, "Other Aromatics," and Aliphatics Measured at the Inlet to the Vacuum Degasser's Control System With Respect to Process Lapse Time

FACILITY	SAMPLING LOCATION	COMPOUND	MEAS. CONC. (ppm)	TIME		
				Start of Treatment Process	Time Sample Taken	Process Lapse Time (min.)
Chevron USA, El Segundo Refinery	Inlet to the Vacuum Degasser Control System	Benzene	400	1058	1144	46
			7,000[a]	"	1655	357
			350[a,b]	"	1655	357
		Other Aromatics	10	"	1144	46
			90[a]	"	1655	357
			3[a,b]	"	1655	357
		Aliphatics	1,100	"	1144	46
			1,600[a]	"	1655	357
			700[a,b]	"	1655	357
PG&E Union City	Inlet to the Vacuum Degasser Control System	Benzene	50	0945	0945	Start Up
			950	"	1256	191
		Other Aromatics	4	"	0945	Start Up
			30	"	1256	191
		Aliphatics	2,700	"	0945	Start Up
			1,900	"	1256	191
Maxwell Labs, San Diego	Inlet to Control Systems	Benzene	18	1625	1640	15
			31	"	2150	325
			50	"	2226	363
			220	"	0012	467

[a] Simultaneous bag sample.

[b] Result not used in the ARB evaluation process because of a suspected leak into this sample bag.

Low vacuum degasser flow rates offset the effect of high concentrations on the pollution mass emission rate. Flow rates measured from the vacuum degasser were very low, especially those measured at the San Diego test, resulting in emission mass rates on the order of 0.1 pounds per hour and less. The uncontrolled and controlled mass rates based on the ARB data are presented in Table 3-9. Benzene, toluene, and the aliphatic hydrocarbons were the only components in the vacuum degasser emissions that were present in amounts significant to a mass emission calculation.

The furnace's exhaust gas flow rate of 267.9 cubic feet per minute was estimated from calculations based on fuel analysis and fuel flow rates. However, benzene and toluene were not detected in the furnace exhaust gas, resulting in zero emissions from the furnace for these two compounds.

At the ARB's request, SUNOHIO left the activated carbon canister in place for the first two tests: the SCAQMD staff tested for emissions at the inlet and outlet of the carbon canister at the first test and the ARB staff tested at the inlet and outlet of the enitre control device during the second test. The PCBX system treated a total of 48,750 gallons of oil at the Chevron USA refinery before being moved to Union City. Depending upon the process flow rate, this would correspond to a continuous treatment time of 54 to 98 hours, or approximately 2 to 4 days.

Based on the SCAQMD's El Segundo test results, adsorber effeciency with respect to PCB was 99 percent during the first 3 hours of oil treatment. Assuming this level of control to be applicable for other aromatics and aliphatics as well, carbon canister breakthrough had not occurred. However, analysis of the ARB's subsequent PG&E data indicates that breakthrough occurred prior to this test. Therefore, sorbent saturation was reached sometime between the conclusion of the SCAQMD's El Segundo test and the start of the ARB's Union City test, a span of 51 to 94 hours of uncertainty. San Diego test data is also indicative that the lifetime of the carbon cartridge is limited to a few hours of PCBX processing time. Upon review of preliminary ARB test data and subsequent tests of their own, SUNOHIO modified its operating schedule to replace the carbon canister after 48 hours of oil treatment processing time. However, more tests are recommended to determine the actual lifetime of the activated carbon for this particular application.

TABLE 3-9

MASS RATE OF BENZENE, TOLUENE, & ALIPHATIC HYDROCARBONS FROM THE VACUUM DEGASSER (ARB Data Only)

FACILITY	SAMPLE LOCATION	FLOW RATE (cfm)	COMPOUND	CONCENTRATION (ppm)	MASS[3] RATE (lbs/hr)
Chevron USA	Inlet to Control System	.545[a]	Benzene[1]	400	.0032
				7,000	.056
			Aliphatic Hydrocarbons[2]	700	.012
				1,600	.028
PG&E	Inlet to Control System	1.55[b]	Benzene[2]	50	.00096
				950	.018
			Aliphatic Hydrocarbons[2]	2,700	.113
				1,600	.028
	Outlet from Control System	1.55[b]	Benzene[2]	600	.011
				700	.013
			Aliphatic Hydrocarbons[2]	1,400	.058
				1,800	.075
Maxwell Labs	Inlet to Condenser/ Carbon Control System	0.03[b]	Benzene	18	6.6×10^{-6}
				31	1.1×10^{-6}
				220	8.1×10^{-5}
				50	1.8×10^{-5}
			Toluene	<0.1	–
				90	3.9×10^{-5}
				290	1.26×10^{-4}
	Outlet from Condenser/ Carbon Control System	0.03[b]	Benzene	10	3.7×10^{-6}
				15	5.5×10^{-6}
				23	8.5×10^{-6}
				20	7.4×10^{-6}
			Toluene	<0.1	–
				<0.1	–
				26	1.1×10^{-5}
	Outlet from Combustion System	257.9[c]	Benzene	<0.1	–
			Toluene	<0.1	–

1 M.W. = 78
2 Assumed to be all C_{12} hydrocarbon, M.W. = 170
3 (ppm) (M.W.) Q (1.58 x 10^{-7} = lbs./hr.)

a (dry) scfm
b (wet) cfm
c Calculated volumetric flow rate. Calculations in APPENDIX V of this report.

FIGURE 3-2

Chevron U.S.A., El Segundo Refinery
Concentrations of Benzene, Other Aromatics & Aliphatic
Measured at the Inlet to the Control Systems
vs.
Process Lapse Time

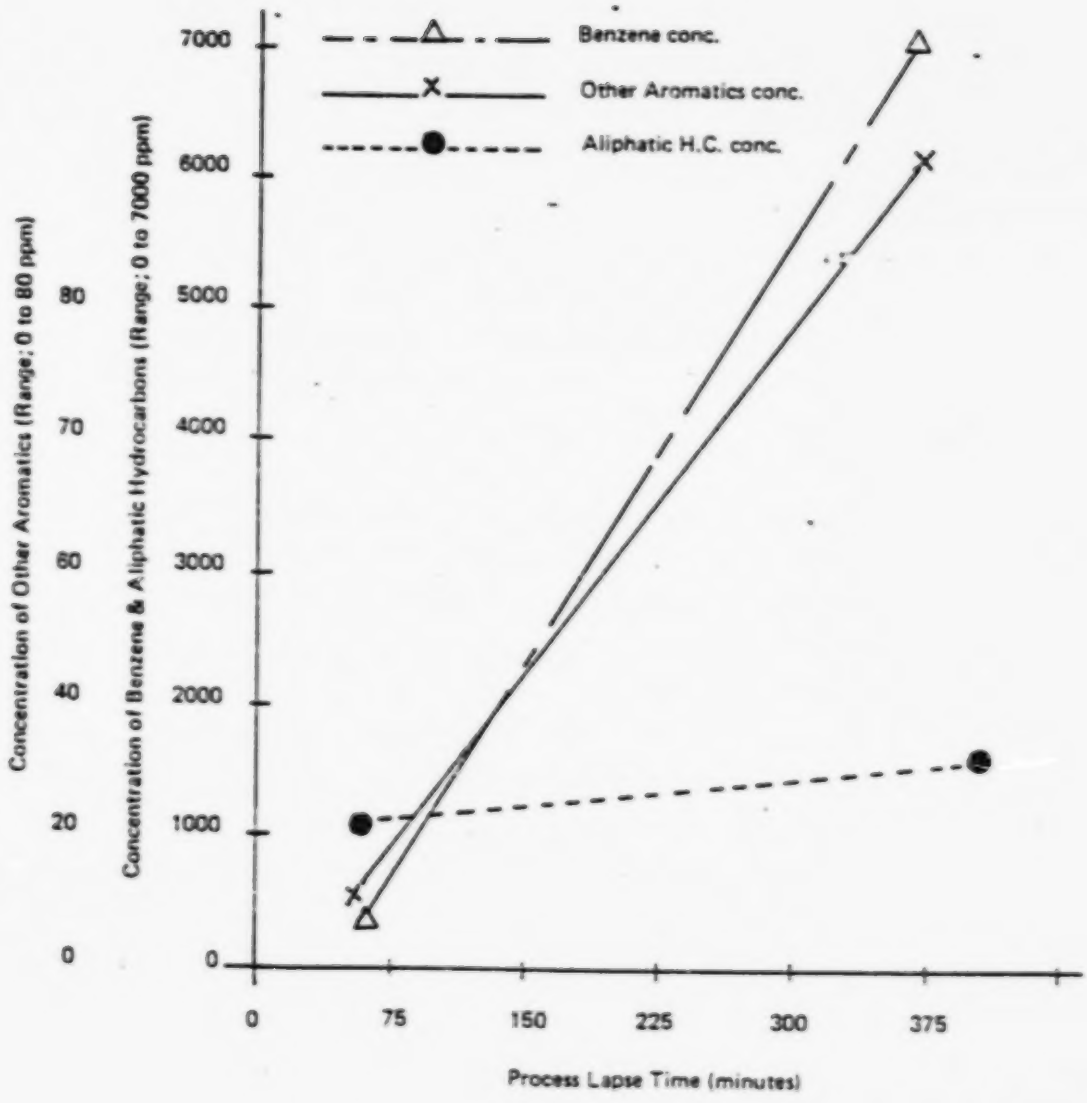


FIGURE 3-3

PG&E, Union City
Concentrations of Benzene, Other Aromatics & Aliphatic
Measured at the Inlet to the Control Systems
vs.
Process Lapse Time

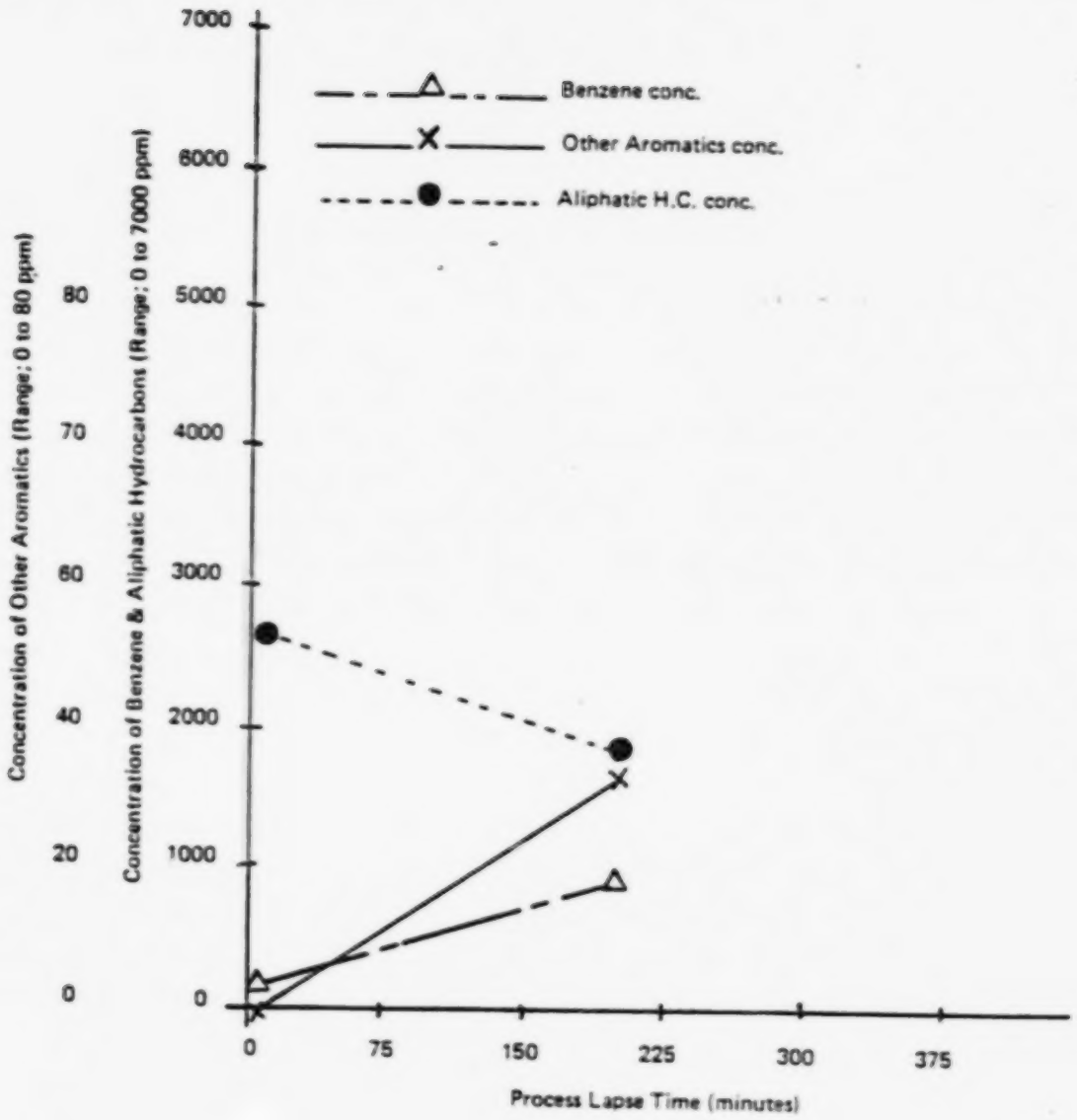
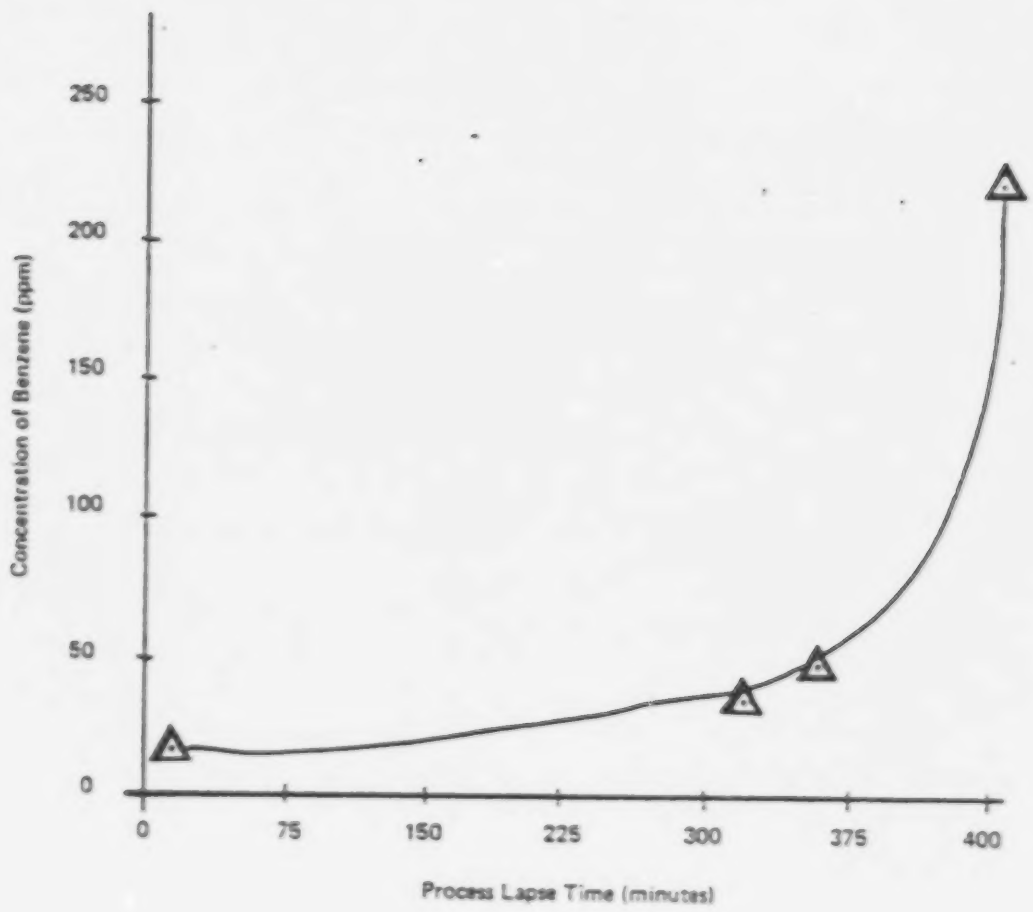


FIGURE 3-4

Maxwell Laboratory, San Diego
Benzene Concentration Measured at the Inlet to the
Control System vs. Process Lapse Time



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3. "Measurement of PCB Emissions from Combustion-Sources;" Levins, P.L., et. al, Arthur D. Little, Inc.; prepared for Industrial Environmental Research Lab, Research Triangle Park, N.C., EPA 600/7-79-047; February 1979.

4. Personal communication with Mr. James Kozak, SUNOHIO.

SECTION 4

COMMERCIAL DEMONSTRATION OF WET AIR OXIDATION OF HAZARDOUS WASTES

SUMMARY

Wet Air Oxidation by Zimpro, Inc., is a process which has been used to oxidize dissolved or suspended organic substances at elevated temperature and pressures. The process is thermally self-sustaining with relatively low organic feed concentrations and is, therefore, most useful for wastes which are too dilute to incinerate economically yet too toxic to treat biologically.

The purpose of this project was to demonstrate wet air oxidation of toxic and hazardous wastes at a full-size installation which was located at Casmalia Resources, a commercial waste treater in California. In the operation of the full-scale Zimpro Wet Air Oxidation unit, wastes selected from classified groups of organic wastes were detoxified. These classified groups were: phenolic wastes, organic sulfur wastes, general organic wastes, cyanide wastes, pesticide wastes, and solvent still bottoms wastes. This section contains detailed evaluation of these six classified wastes' treatment, the effectiveness of the wet air oxidation unit, and sample analysis of feed and effluent.

Oxidation of a petroleum refining spent caustic waste resulted in 99.77 percent total phenol reductions, 94.0 percent organic sulfur reduction, and 89.3 percent chemical oxygen demand [COD] reduction. Oxidation of spent caustic wastewater from a petroleum refinery resulted in sulfide reduction of >99.7 percent, phenol reduction of 98.8 percent, and COD reduction of 81.3 percent. Very effective treatment of the general organic waste was obtained by wet air oxidation. Oxidation resulted in 96.7 percent COD reduction. However, an increase in soluble chloride concentration in the oxidized effluent was observed following wet air oxidation. In case of cyanide experimentation, 99.7 percent reduction of cyanide and 88.8 percent reduction in COD were observed upon completion of wet air oxidation. High levels of destruction—98.0 to greater than 99.8 percent—were observed for the full-scale wet air oxidation of four pesticides. COD and BOD removals of 72.3 and 73.6 percent were observed in a full-scale wet air oxidation demonstration of a solvent still bottoms type wastewater.

INTRODUCTION

Zimpro, Inc., has been granted an EPA-funded contract through the State of California, Department of Health Services, for the purpose of demonstrating wet air oxidation of toxic and hazardous wastes at a full-scale installation located at Casmalia Resources, Inc., a secure chemical waste landfill in Santa Barbara County, California. This report includes operating and performance data obtained during demonstration of wet air oxidation of six classified groups of wastes.

DESCRIPTION OF WET AIR OXIDATION PROCESS

The Zimpro Wet Air Oxidation unit for this demonstration processed aqueous wastes at a designed reactor temperature of 550°F, a designed reactor pressure of 2,000 psig a liquid waste flow rate of 10 GPM, and a compressed air rate of approximately 190 SCFM. In the wet oxidation process, liquid waste, exiting from a high pressure pump, is combined with compressed air and directed through the cold, heat-up side of the heat exchanger. The incoming waste-air mixture exits from the heat-up side of the heat exchanger and enters the reactor where exothermic reactions increase the temperature of the mixture to a desired value. The waste-air mixture exits the reactor and enters the hot, cool-down side of the heat exchanger and, after passage through the system pressure control valves, is directed to the separator. In the separator, the spent process vapors (noncondensible gases) are separated from the oxidized liquid phase and are directed into a two-stage water scrubber-carbon bed adsorber, vapor treatment system.

In the wet air oxidation process, organic substances can be completely oxidized to yield highly oxygenated products and water. For example, organic carbon-hydrogen compounds can be oxidized to carbon dioxide and water, while reduced organic sulfur compounds (sulfides, mercaptans, etc.) and inorganic sulfides are easily oxidized to inorganic sulfate, usually present in the oxidized liquor as sulfuric acid. Inorganic cyanides and organic cyanides (nitriles) are easily oxidized to carbon dioxide, ammonia, or molecular nitrogen. It should be noted that oxides of nitrogen such as NO or NO_2 are not formed in wet air oxidation.

When incomplete oxidation of organic substances occurs, the easily oxidized reduced sulfur and cyanides are usually still oxidized to sulfate and carbon dioxide-ammonia provided a sufficient degree of oxidation is accomplished. However, incomplete oxidation of other organic compound results in the formation of low molecular weight compounds such as acetaldehyde, acetone, and acetic acid. These low molecular weight compounds are volatile and are distributed between the process off-gas phase and the oxidized liquid phase. The concentration of these low molecular

weight compounds (measured as total hydrocarbons (THC) expressed as methane) in the process of off-gas is dependent on their concentration in the oxidized liquid phase, which is determined by the degree of oxidation accomplished, the waste being oxidized, and the influent organic concentration of the waste.

A. PHENOLIC AND ORGANIC SULFUR WASTE CLASSES

Summary and Conclusion

Wet air oxidation of phenolic and organic sulfur classes of waste has been demonstrated at the Casmalia Resources, Inc., full-scale wet air oxidation installation. Oxidation of a petroleum refining spent caustic waste at a process temperature of 515°F (268°C) and a nominal residence time of 113 minutes resulted in 99.77 percent total phenols reduction, 94.0 percent organic sulfur reduction, and 89.3 percent chemical oxygen demand (COD) reduction. Gas chromatographic/mass spectroscopic (GC-MS) analysis identified acetic acid, benzoic acid, and several sulfide derivatives as the major components present in the effluent oxidized waste. Analysis of treated process off-gases indicated a total hydrocarbon (THC) concentration of only 84.5 ppm (expressed as methane).

Therefore, performance data obtained during full-scale oxidation of the spent caustic waste demonstrates wet air oxidation to be effective for treatment of wastewaters in the phenolic and organic sulfur classes of waste.

Demonstration Program

1. Operating Conditions

The wet air oxidation demonstration of petroleum refining spent caustic waste was performed during an eight-hour period of operation at steady state conditions on May 19, 1983. During the demonstration period, the wet air oxidation unit was operated at an average reactor temperature of 515°F (268°C), a compressed air rate of 190 SCFM, and a reactor pressure of 1,610 psig. Waste was processed at a liquid flow rate of 5.3 GPM corresponding to a nominal residence time of 113 minutes. Residual oxygen concentrations in the process off-gas averaged 3.7 percent during the demonstration period.

2. Sampling Procedures

Sampling procedures used during the wet air oxidation demonstration period were performed according to the sampling program outlined in the Proposal for U. S. EPA Commercial Scale Demonstration Wet Oxidation of Hazardous Waste.[1] Liquid composites of the influent raw waste and the effluent oxidized waste were obtained by collecting one-liter samples of each stream on an hourly interval throughout the demonstration period. Samples were composited in thoroughly cleaned, five-gallon stainless steel containers.

Upon completion of the demonstration period, split samples of the composite streams were transferred to one-liter glass jars. Composite feed and effluent samples were then returned to Zimpro, Inc., for analyses. A one-liter composite sample of each stream was also retained on-site and made available to the EPA for analysis.

Duplicate off-gas grab samples were obtained from the wet air oxidation unit during the demonstration period. Off-gases were sampled after treatment but prior to discharge to the atmosphere. One off-gas sample was analyzed on-site by Zimpro personnel for oxygen, nitrogen, carbon dioxide, carbon monoxide, total hydrocarbons, and methane. The remaining off-gas sample was retained on-sits and made available to the EPA for analysis.

3. Analytical Procedures

Procedures used by Zimpro, Inc., for analysis of the composite influent raw waste, composite effluent oxidized waste, and grab off-gas sample are contained in the Quality Assurance Project Plan[2] for the commercial demonstration of wet air oxidation of hazardous wastes.

Gas chromatographic/mass spectroscopic (GC-MS) analysis of composite raw and oxidized waste samples were performed using a Finnigan 4021 GC-MS. Aliquots of each sample were placed in 40 ml vials and sealed with a Teflon-lined septum such that no air bubbles were present. The 40 ml vial samples were then screened for volatile compounds

by direct injection using a 6' x 2 mm 1% SP-1000 on CP-C packed column (1 min. @ 50°C, 10°C/min. to 220°C) to chromatograph the volatile components.

Additional volumes of the raw and oxidized waste samples were extracted with methylene chloride according to EPA Method 625[3] for the acid and base-neutral fractions. The raw waste acid fraction extract was concentrated to a final volume of 50 ml while the base-neutral fraction extract was concentrated to 10 ml. Both oxidized waste extracts were concentrated to a final volume of 2.0 ml. The acid extracts were then chromatographed on a 6' x 2 mm 1% SP-1240 DA on Supelcoport packed column (2 minutes at 70°C, 8°C/min. to 200°C). Base-neutral extracts were chromatographed on a 6' x 2 mm 3% SP-2250 DB on Supelcoport (4 minutes at 45°, 8°/min. to 270°C).

Results and Discussion

1. Waste Selection

The waste selected for the wet air oxidation demonstration run was obtained from a petroleum refinery located in California. Previous laboratory screening tests consisting of treatability and materials of construction testing indicated the waste to be acceptable for treatment by wet oxidation.[4]

The waste selected is a spent caustic waste generated by various petroleum refining processes and contains high concentrations of phenolic and organic sulfur compounds. Since both phenols and organic sulfur compounds are present in the waste, this demonstration run was used to determine treatment by wet air oxidation of both the phenolic and organic sulfur classes of wastes.

2. Performance Results

Analyses of the composite feed and effluent samples collected during the demonstration period are reported in Table I. The composite feed had a chemical oxygen demand (COD) of 108.1 g/l and a pH of 13.0. Total phenols and organic sulfur concentrations of the composite feed were 15,510 and 3,010 mg/l, respectively.

Wet air oxidation resulted in very effective treatment of the spent caustic waste. COD of the composite feed was reduced to 11.6 g/l in the composite effluent representing a COD

reduction of 89.3 percent. A total phenols reduction of 99.77 percent was achieved with only 36 mg/l residual total phenols observed in the oxidized effluent. Oxidation resulted in good conversion of organic sulfur to sulfate sulfur with sulfur data indicating an organic sulfur reduction of 94.0 percent.

The pH of the spent caustic waste decreased from 13.0 to 8.3 upon oxidation. Similar pH decreases are typically observed during wet oxidation of wastes containing reduced sulfur compounds. Oxidation of these materials results in the formation of inorganic sulfate, normally present as sulfuric acid, resulting in a decreased pH in the oxidized effluent.

Soluble chloride analyses indicated an apparent decrease from 1,510 to 550 mg/l following oxidation. Similar results were observed during laboratory screening of the spent caustic waste and have been observed during past industrial waste oxidation studies. This apparent decrease in soluble chloride is likely due to the presence of materials in the raw waste which exert a positive interference during the chloride analysis. Oxidation of these materials eliminates the interference and should result in an accurate chloride analysis for the oxidized waste.

3. GC-MS Analysis

GC-MS analysis was performed on the composite feed and effluent samples obtained during the petroleum refinery spent caustic waste demonstration run. Compounds identified during analysis of the volatile, acid, and base-neutral fractions of the feed and effluent samples are reported in Tables 4-2A to 4-7A.

Major volatile components identified in the composite feed sample include phenol, methylphenol isomers, and a few sulfides. Volatile components in the effluent sample were composed primarily of acetic acid. Phenol, methylphenol isomers, and dimethylphenol isomers were the major components identified in the feed acid fraction extract. Benzoic acid and methylbenzoic acid isomers were the major components of the effluent acid fraction extract. Although wet chemical analysis indicated 36 mg/l total phenols in the effluent composite sample, no phenols were identified in the effluent acid fraction extract. Several peaks in the effluent acid extract were not identified and may

be phenolic compounds which are not included in the GC-MS library. Many of the feed components of the base-neutral fraction extract could not be identified by the GC-MS library. The effluent base-neutral fraction extract contained several sulfide derivatives.

4. Process Off-Gas Analysis

A grab sample of the wet air oxidation unit process off-gas was collected during the demonstration period. The sample was collected at a point after treatment but prior to discharge to the atmosphere. Results of chromatographic analysis of the off-gas sample are reported in Table 4-8A. Analysis of the off-gas indicated carbon dioxide, oxygen, and nitrogen concentrations of 11.3, 4.3, and 83.2 percent, respectively. Carbon monoxide was not detected in the off-gas sample.

A total hydrocarbon (THC) concentration of 85.4 ppm (expressed as methane) and a methane concentration of 12.1 ppm were determined for the process off-gas sample. Results of off-gas analysis by an on-line continuous THC analyzer (Beckman, Model 400 THC Analyzer) indicated a THC concentration of 80 ppm at the approximate time the grab off-gas sample was collected.

REFERENCES

1. *Proposal for U. S. EPA Commercial Scale Demonstration Wet Oxidation of Hazardous Waste*, Zimpro, Inc., June 1982.

2. *Quality Assurance Project Plan, Commercial Demonstration Wet Air Oxidation of Hazardous Waste, Casmalia Resources, California*, Zimpro, Inc., February 16, 1983.

3. "EPA Method 625," *Federal Register*, December 3, 1979.

4. Dietrich, J. J., "Casmalia Resources Wet Air Oxidation Unit Screening; Petroleum Refinery Spent Caustic Wastewater," January 18, 1983.

TABLE 4-1A

WET AIR OXIDATION DEMONSTRATION
PETROLEUM REFINERY SPENT CAUSTIC WASTEWATER

Wet Air Oxidation Conditions:

Oxidation Temperature	515°F (268°C)
Nominal Residence Time	113 min.
Waste Flow Rate	5.3 GPM
Compressed Air Flow Rate	190 SCFM
Reactor Pressure	1,610 PSIG
Residual Oxygen Concentration	3.7%

SAMPLE DESCRIPTION	COMPOSITE INFLUENT RAW WASTE	COMPOSITE EFFLUENT OXIDIZED WASTE
COD, g/l	108.1	11.6
COD Reduction, %	–	89.3
Total Phenols, mg/l	15,510	36
Total Phenols Reduction, %	–	99.77
Total Sulfur, mg/l	3,580	3,090
Sulfate Sulfur, mg/l	570	2,910
Organic Sulfur, mg/l*	3,010	180
Organic Sulfur Reduction, %	–	94.0
Sulfide Sulfur, mg/l	1.0	1.0
pH	13.0	8.3
Total Solids, g/l	88.6	59.7
Total Ash, g/l	57.1	50.2
Volatile Solids, g/l	31.5	9.5
DOC, mg/l	–	3,680
Soluble Chloride, mg/l	1,510	550
Soluble Fluoride, mg/l	4.4	1.3

* Organic Sulfur = Total Sulfur Minus Sulfate Sulfur.

TABLE 4-2A

CASMALIA SPENT CAUSTIC FEED VOLATILE REACTION

SCAN NUMBER	COMPOUND
55	Methanethiol
147	Ethanediol
349	Dimethyldisulfide
455	?
575	Phenol
733	Column Bleed
823, 889, 928	Methyl phenol isomers

TABLE 4-3A

CASMALIA SPENT CAUSTIC OXIDIZED VOLATILE FRACTION

SCAN NUMBER	COMPOUND
106	Ethanol
137	Methylene Chloride
285	Acetic acid
523	Propanedioic acid
733	Column Bleed

TABLE 4-4A

CASMALIA SPENT CAUSTIC FEED ACID FRACTION

SCAN NUMBER	COMPOUND
56	Benzenethiol
101	2-Methyl-benzenethiol
131, 140, 148, 171, 210	?
235	Phenol
245, 274	Methylphenol isomers
300, 309, 323	Dimethylphenol isomers
336	Propylphenol
351	4-Ethyl-2-methylphenol
369, 389	Dimethylbenzaldehyde
374	Trimethylphenol

TABLE 4-5A

CASMALIA SPENT CAUSTIC OXIDIZED ACID FRACTION

SCAN NUMBER	COMPOUND
36	Solvent
69	Propanoic acid
138	Hydroxybenzaldehyde
162	Butanoic acid
194	3,4-Dimethyl-2,5-furandione
244	Sulfonylbis-methane
392, 410	Methylbenzoic acid ixomers
492	?
506	Hydroxybenzoic acid
516	Hydroxybenzaldehyde
526, 552, 630, 729	?
366	Benzoic acid

TABLE 4-6A

CASMALIA SPENT CAUSTIC
FEED BASE/NEUTRAL FRACTION

SCAN NUMBER	COMPOUND
32	Solvent
60	?
223	Diethyldisulfide
267	Dimethyltrisulfide
320	Methylpyridine or benzenamine
353	Methylbenzenamine
360, 392	Dimethylphenol
383	4-Methyl-2-pyridinamine
414	Dimethylphenol and ?
456, 495, 507, 526	?
694, 720	?

TABLE 4-7A

CASMALIA SPENT CAUSTIC OXIDIZED
BASE/NEUTRAL FRACTION

SCAN NUMBER	COMPOUND
33	Solvent
220	Pyridine
297	Benzofuran
328	Benzaldehyde
356	3-Phenyl-2-propenal or 7-Methylbenzo-furan
383	Methylbenzaldehyde
407	Sulfonylbismethane ?
462	Methylbenzo[b] thiophene
473	Quinoline or isoquinoline
492	Aliphatic hydrocarbon
507	2(1H)-Quinolinone + 1(2H)-Phthalazincne ?
537	Methylsulfonylbenzene
573	[(Methylsulfonyl)methyl] benzene ?
585	4-Methylbenzenesulfonamide
698	9H-Xanthen-9-one
723	4-Methoxybenzo[c] cinnoline
753	1,2-Dihydro-2-phenyl-3H-indazol-3-one

TABLE 4-8A

WET AIR OXIDATION DEMONSTRATION
PETROLEUM REFINERY SPENT CAUSTIC WASTEWATER

PROCESS OFF-GAS ANALYSIS

Carbon Dioxide	11.3%
Oxygen	4.3%
Nitrogen	83.2%
Carbon Monoxide	Not Detected
Methane	12.1 ppm
Total Hydrocarbons	85.4 ppm as methane

B. PETROLEUM REFINERY SPENT CAUSTIC WASTEWATER

Summary

Wet air oxidation at 280°C for 60 minutes has been performed on a sulfide and phenol containing spent caustic wastewater from a petroleum refinery located in California. Oxidation resulted in sulfide reduction of >99.7 percent, phenols reduction of 98.8 percent, and COD reduction of 81.3 percent. Materials of construction studies indicated compatibility with titanium.

Thus, treatability and materials of construction testing indicate the petroleum refinery spent caustic wastewater to be an acceptable candidate for treatment in the Casmalia wet air oxidation system.

Discussion

Treatability

Laboratory autoclave wet air oxidation has been performed on a petroleum refinery spent caustic wastewater at the Casmalia wet oxidation unit nominal operating conditions of 280°C for 60 minutes. The waste as received had a high COD (151.0 g/l) and was diluted to 40.0 g/l COD prior to oxidation. Treatability by wet oxidation was determined by sulfide, phenols, and COD reductions.

Oxidation resulted in >99.7 percent sulfide sulfur reduction, 98.8 percent total phenols reduction, and 81.3 percent COD reduction. Sulfide sulfur and total phenols concentrations were reduced to >1.0 mg/l and 66 mg/l, respectively, upon oxidation. Further reduction in residual total phenols concentration would likely be achieved by postoxidation treatment with ozone or hydrogen peroxide.

The raw spent caustic wastewater had a BOD_5/COD ratio of 0.49 compared to 0.64 for the oxidized product indicating a slight increase in biodegradability following oxidation. The oxidized product would likely be easily biodegradable since highly biodegradable materials generally have BOD_5/COD ratios in the range of 0.5 to 0.6.

The wastewater pH decreased from 12.6 in the raw waste to 8.7 upon oxidation, likely due to the conversion of reduced sulfur compounds to sulfuric acid.

An apparent decrease in soluble chloride concentrations from 2,190 mg/l in the diluted feed to 470 mg/l in the oxidized product was observed following wet oxidation. Similar results have been observed with previous industrial waste oxidation studies and are likely due to a positive chloride interference in the raw wastewater caused by organic or reduced inorganic materials. Oxidation of these materials should result in a more accurate chloride analysis for the oxidized product.

Oxidation results and analytical data are reported in Table 4-18.

Materials of Construction Compatibility

Autoclave corrosion tests were performed at 140°C for 70 hours and 280°C for 90 hours to determine the effects of partial and complete oxidation on titanium. No localized corrosion was observed at either condition. A general corrosion rate of 2.5 mils per year was determined at 280°C. Carbon steel tanks with Ceilcote lining 103 are recommended for on-site storage of the spent caustic wastewater.

Hazardous Waste Compatibility

A hazardous waste compatibility chart is attached to this report. Materials capable of hazardous reactivity with the major components of the spent caustic wastewater—sulfides, phenols, and caustic—are indicated.

Experimental

Oxidation was performed using a titanium laboratory autoclave. The autoclave was charged with 100 ml diluted feed and air containing oxygen in excess of the sample oxygen demand, placed in a heater/shaker mechanism, heated to 280°C, and held at temperature for 60 minutes. The autoclave was cooled with tap water immediately after oxidation.

For corrosion testing, as-welded titanium samples were exposed to the diluted waste. A 150 ml sample was charged to a titanium autoclave containing the titanium corrosion samples.

The test was then run at 140°C for 70 hours. After completion of this test, a new titanium coupon was exposed to a new waste sample at 280°C for 90 hours. After test completion, general corrosion rates were determined and samples were evaluated for localized corrosion.

Oxidation off-gases were analyzed by gas chromatography. Other analyses reported in Table 4-1B were performed according to *Standard Methods*.[1]

REFERENCES

1. *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA, WPCF, 15th Ed., 1980.

2. Zimpro Research Notebook No. 2082, p. 8.

Table 4-1B

PETROLEUM REFINERY SPENT CAUSTIC WASTEWATER
WASTE CODE NO. 5003

SAMPLE DESCRIPTION	WASTE AS RECEIVED	DILUTED* FEED	OXIDATION PRODUCT
Oxidation Temperature, °C	–	–	280
Time at Temperature, min.	–	–	60
COD, g/l	151.0	40.0	7.5
COD Reduction, %	–	–	81.3
O_2 Used, g/l	–	–	31.7
AOD, g/l**	–	–	39.2
Total Phenols, mg/l	20,200	5,350	66
Total Phenols Reduction, %	–	–	98.8
Total Sulfur, mg/l	12,260	3,250	3,430
Sulfate Sulfur, mg/l	1,890	500	2,610
Sulfide Sulfur, mg/l	1,440	382	<1.0
Sulfide Sulfur Reduction, %	–	–	>99.7
BOD_5, mg/l	74,600	19,770	4,830
BOD_5/COD, g/g/	0.49	0.49	0.64
pH	12.6	–	8.7
Soluble Chloride, mg/l	8,280	2,190	470
Total Solids, g/l	232.3	61.6	60.7
Total Ash, g/l	201.8	53.5	53.7
Volatile Solids, g/l	30.5	8.1	7.0
Off-gas CH_4, ppm	–	–	5.0
Off-gas THC, ppm	–	–	201
Sample No.	5003-3-1-1 2082-8-1		5003-3-1-2 2082-8-2

* Calculated values based on 265 to 1,000 ml dilution of raw wastewater.
** Autoclave Oxygen Demand = O_2 Used + Residual COD.

C. GENERAL ORGANIC WASTE CLASS

INTRODUCTION

An eight-hour wet air oxidation demonstration of a general organic wastewater was performed at the Casmalia Resources, Inc., full-scale wet oxidation installation on July 28, 1983.

This report contains operating conditions and performance results obtained during the wet air oxidation demonstration. GC-MS analyses of the influent raw waste and effluent oxidized waste samples have not been completed, and therefore, GC-MS results are not included in this report. A detailed interim report discussing the complete general organic wastewater category wet air oxidation demonstration will be prepared by Zimpro, Inc., when GC-MS analyses of the composite waste samples are completed.

Results and Discussion

The wastewater processed during the wet air oxidation demonstration was generated by a polyester resin manufacturing process and was assigned to the general organic wastewater category. The waste was expected to contain high concentrations of propylene glycol and various mixed organic ethers and esters. Previous laboratory screening tests performed by Zimpro, Inc., indicated the waste to be treatable by wet air oxidation and also compatible with respect to materials of construction.

The general organic wastewater was processed continually during the eight-hour wet air oxidation demonstration. During the demonstration period, the wet air oxidation unit was operated at an average reactor temperature of 531°F (277°C), a compressed air flow rate of 190 SCFM and a reactor pressure of 1,515 psig. Waste was processed at an average liquid flow rate of 5.0 GPM resulting in a nominal residence time of 120 minutes. Residual oxygen concentrations in the process off-gas averaged 4.1 percent during the demonstration period.

Analyses of the composite feed and effluent samples obtained during the wet air oxidation demonstration are shown in Table 4-1C. The data indicates the waste to be relatively high strength with a chemical oxygen demand (COD) of 76.0 g/l and a dissolved organic carbon (DOC) concentration of 20,830 mg/l. The raw waste had a pH of 1.9.

Very effective treatment of the general organic waste was obtained by wet air oxidation. Oxidation resulted in 96.7 percent COD reduction with the waste COD reduced to 2.5 g/l. A DOC reduction of 96.7 percent was obtained with the oxidized waste having a DOC concentration of 685 mg/l.

An increase in soluble chloride concentrations from 212 mg/l for the raw waste to 880 mg/l in the oxidized effluent was observed following wet air oxidation. Similar results were observed during the initial laboratory screening of the waste and may be due to the presence of chlorinated organic materials in the raw waste which are broken down during oxidation releasing free chloride.

Results of analysis of a process off-gas grab sample collected during the wet air oxidation demonstration are shown in Table 4-2C. Analysis of the off-gas sample indicated carbon dioxide, oxygen, nitrogen, and carbon monoxide concentrations of 12.9, 5.9, 81.2, and 0.3 percent, respectively. Total hydrocarbon (THC) and methane concentrations of 29.1 ppm (expressed as methane) and 10.0 ppm, respectively, were determined for the process off-gas sample.

Table 4-1C

WET AIR OXIDATION DEMONSTRATION
GENERAL ORGANIC WASTEWATER CLASS

Wet Air Oxidation Conditions:

Oxidation Temperature	531°F (277°C)
Nominal Residence Time	120 min.
Waste Flow Rate	5.0 GPM
Compressed Air Flow Rate	190 SCFM
Reactor Pressure	1,515 PSIG
Residual Oxygen Concentration*	4.1%

Sample Description	Composite Influent Raw Waste	Composite Influent Oxidized Waste
COD, g/l	76.0	2.5
COD Reduction, %	–	96.7
DOC, mg/l	20,830	685
DOC Reduction, %	–	96.7
pH	1.9	3.3
Total Solids, g/l	10.0	3.1
Total Ash, g/l	0.7	1.1
Volatile Solids, g/l	9.3	2.0
BOD_5, mg/l	29,680	880
BOD_5/COD, g/g	0.39	0.39
Soluble Chloride, mg/l	212	866
Soluble Fluoride, mg/l	0.7	<0.5

Table 4-2C

WET AIR OXIDATION DEMONSTRATION
GENERAL ORGANIC WASTEWATER CLASS

Process Off-Gas Analysis

Carbon Dioxide	12.9%
Oxygen	5.9%
Nitrogen	81.2%
Carbon Monoxide	0.3%
Methane	10.0 ppm
Total Hydrocarbons	29.1 ppm as methane

D. CYANIDE WASTE CLASS

INTRODUCTION

Treatment of cyanide wastewaters by wet air oxidation has been demonstrated at the Casmalia Resources, Inc., full-scale wet air oxidation installation. The wet air oxidation demonstration was performed on July 29 and August 18, 1983 during a combined six-hour period of steady state operation.

Operating conditions and performance results obtained during treatment of the cyanide wastewater are discussed in this report. GC-MS analyses of composite raw and oxidized waste samples are currently being performed and results are therefore not included in this report. A detailed interim report discussing the complete wet air oxidation demonstration of the cyanide wastewater will be prepared by Zimpro, Inc., when GC-MS results are available.

Results and Discussion

The wastewater processed during the wet air oxidation demonstration was a mixture of cyanide wastes generated by various metal plating processes. Laboratory screening tests performed by Zimpro, Inc., indicated the individual wastes contained in the wastewater mixture to be treatable by wet air oxidation and compatible with respect to materials of construction.

The cyanide waste treatment demonstration consisted of a four-hour period of steady state operation on July 29, 1983 and a two-hour period of steady state operation on August 18, 1983. The short process runs obtained during treatment of the cyanide waste was due to the presence of high concentrations of metal-cyanide complexes in the waste. As the cyanide waste was processed through the wet air oxidation system, the soluble metal-cyanide complexes were destroyed, resulting in precipitation of the metals. The precipitated metals caused scale formation in the oxidation system which required processing of the waste to be discontinued in order to remove the scale from the system. Therefore, the cyanide waste wet air oxidation demonstration was limited to two separate periods of operation for a combined total of six hours treatment at steady state operating conditions.

During the combined demonstration period, the wet air oxidation unit was operated at an average reactor temperature of 495°F (257°C), a compressed air flow rate of 190 SCFM,

and a reactor pressure of 1,220 psig. Waste was processed at an average liquid flow rate of 7.5 GPM, resulting in a nominal residence time of 80 minutes. Residual oxygen concentrations in the process off-gas averaged 7.1 percent during the demonstration period.

Analyses of the influent raw waste and effluent oxidized waste samples composited during the demonstration are reported in Table 4-1D. The analyses indicate the composite raw waste to be a typical high strength cyanide waste with a cyanide concentration of 25,390 mg/l, chemical oxygen demand (COD) of 37.4 g/l, and pH of 12.6.

Wet air oxidation resulted in very effective treatment of the cyanide waste. The cyanide concentration of the raw waste was reduced to 82 mg/l, representing a cyanide reduction of 99.7 percent. A COD reduction of 88.8 percent and a dissolved organic carbon (DOC) reduction of 88.4 percent were obtained by wet air oxidation. COD and DOC concentrations in the composite oxidized waste were 4.2 g/l and 1,710 mg/l, respectively.

The scale formation which occurred in the oxidation unit during the cyanide demonstration period is reflected by the total ash data. The composite raw waste had a total ash concentration of 112.9 g/l compared to only 77.4 g/l for the composite oxidized waste. Since the ash is expected to pass through the oxidation unit as inert material, the data indicates as much as 35 g/l of inert solids were deposited in the oxidation system during treatment of the cyanide waste.

Results of analysis of a process off-gas grab sample collected during the demonstration period are shown in Table 4-2D. Analysis of the off-gas sample indicated 1.5 percent carbon dioxide, 8.5 percent oxygen, and 82.8 percent nitrogen. Carbon monoxide was not detected in the off-gas sample. A total hydrocarbon (THC) concentration of 61.1 ppm (expressed as methane) and a methane concentration of 9.0 ppm was determined for the process off-gas sample.

GC-MS analyses are currently being performed on the composite raw waste and oxidized waste samples. Results of these analyses will be published by Zimpro, Inc., in a detailed interim report which will be prepared following completion of GC-MS testing.

Table 4-1D

WET AIR OXIDATION DEMONSTRATION
CYANIDE WASTEWATER CLASS

Wet Air Oxidation Conditions:

Oxidation Temperature	495°F (257°C)
Nominal Residence Time	80 min.
Waste Flow Rate	7.5 GPM
Compressed Air Flow Rate	190 SCFM
Reactor Pressure	1,220 PSIG
Residual Oxygen Concentration	7.1%

Sample Description	Composite Influent Raw Waste	Composite Influent Oxidized Waste
COD, g/l	37.4	4.2
COD Reduction, %	–	88.8
Cyanide, mg/l	25,390	82
Cyanide Reduction, %	–	99.7
DOC, mg/l	14,710	1,710
DOC Reduction, %	–	88.4
pH	12.6	9.0
Total Solids, g/l	135.3	91.2
Total Ash, g/l	112.9	77.4
Volatile Solids, g/l	22.4	13.8
BOD_5, mg/l	–	603
Soluble Chloride, mg/l	–	773
Soluble Fluoride, mg/l	30	29

Table 4-2D

WET AIR OXIDATION DEMONSTRATION
CYANIDE WASTEWATER CLASS

Process Off-Gas Analysis

Carbon dioxide	1.5%
Oxygen	8.5%
Nitrogen	82.8%
Carbon Monoxide	Not Detected
Methane	9.0 ppm
Total Hydrocarbons	61.1 ppm as methane

E. PESTICIDE WASTE CLASS

SUMMARY

High levels of destruction—98.0 to greater than 99.8 percent—were observed for the full-scale wet air oxidation of four pesticides in the Casmalia Resources wet air oxidation unit. Dinoseb, methoxychlor, carbaryl, and malathion were added to an acidic distillate waste which had previously been processed in the Casmalia wet air oxidation unit.

An eight-hour wet air oxidation demonstration of a pesticide containing wastewater was performed at the Casmalia Resources, Inc., full-scale wet air oxidation installation on March 28, 1984. This report contains operating conditions and performance results obtained during the wet air oxidation demonstration.

Results and Discussion

Wet air oxidation of four pesticides—dinoseb, methoxychlor, carbaryl, and malathion—was evaluated in a full-scale demonstration at Casmalia Resources, Casmalia, California, on March 28, 1984. Since wastewaters containing relatively high concentrations of a variety of pesticides were not easily available, the above compounds were spiked into an acidic distillate wastewater which had previously been processed in the Casmalia wet air oxidation unit.

Prior to the full-scale pesticides wet air oxidation demonstration, bench scale autoclave oxidations of a variety of pesticides had been evaluated. Results of these screening tests, also performed in the acidic distillate wastewater matrix, are reported in Table 4-1E. Greater than 99 percent destruction was observed for seven pesticides, including the four subsequently demonstrated in the Casmalia full-scale unit.

The pesticide wastewater was processed continuously during the eight-hour wet air oxidation demonstration. During the demonstration period, the wet air oxidation unit was operated at an average reactor temperature of 537°F (280°C), a compressed air flow rate of 190 SCFM, and a reactor pressure of 1,600 psig. Waste was processed at an average liquid flow rate of 3.3 GPM, resulting in a nominal residence time of 182 minutes. Residual oxygen

concentrations in the process off-gas averaged 2.3 percent during the demonstration period. Feed and effluent composite samples were prepared by combining hourly grab samples from each sampling point.

Analyses of the composite feed and effluent samples obtained during the wet air oxidation demonstration are shown in Table 4-2E. Removals of the four pesticides ranged from 98.0 to greater than 99.8 percent. Analyses of pesticides in the feed and effluent composites were by gas and liquid chromatography. Due to an interference in the gas chromatographic analysis of effluent malathion, this compound was quantified using GC-MS techniques.

COD, BOD_5, and DOC removals were quite similar to results obtained during oxidation of the acidic distillate waste alone.[1] COD, BOD_5, and DOC removals of 95.3, 93.8, and 96.1 percent were observed.

Results of gas chromatographic analyses of a process off-gas grab sample collected during the wet air oxidation demonstration are shown in Table 3. Carbon dioxide, oxygen, nitrogen, and carbon monoxide concentrations of 14.2, 3.5, 79.0, and 0.7 percent, respectively, were observed. Total hydrocarbon (THC) and methane concentrations of 153 ppm (expressed as methane) and 61.9 ppm, respectively, were determined for the process off-gas sample.

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1 Dietrich, M. J., "Commercial Demonstration of Wet Air Oxidation of Hazardous Wastes: General Organic Waste Class," October 17, 1983, Zimpro, Inc., Interim Report.

Table 4-1E

*WET AIR OXIDATION DESTRUCTION OF PESTICIDES ADDED TO ACIDIC DISTILLATE WASTE

Pesticide	**Feed, mg/l	Oxidation Product, mg/l	% Destruction
DBCP	42.5	0.28	99.3
Malathion	39.5	<0.3	<99.2
Carbaryl (sevin)	53.5	<0.1	<99.8
Carbofuran (Furadan)	46.5	<0.1	<99.8
Dinoseb	65.0	<0.1	<99.8
Methoxychlor	77.3	<0.1	<99.9
Linuron (Lorox)	87.0	<0.1	<99.9

* Oxidation at 280°/60 minutes.

** Compounds added to acidic distillate waste which had been diluted 1 to 4.

Table 4-2E

WET AIR OXIDATION DEMONSTRATION
PESTICIDE WASTE CLASS

Wet Air Oxidation Conditions:

Oxidation Temperature	537°F
Nominal Residence Time	182 min.
Waste Flow Rate	3.3 GPM
Compressed Air Flow Rate	190 SCFM
Reactor Pressure	1,600 PSIG
Residual Oxygen Concentration	2.3%

Sample Description	Composite Influent Raw Waste	Composite Influent Oxidized Waste
Dinoseb, mg/l	37.1	0.19
Dinoseb Reduction, %	–	99.5
Methoxychlor, mg/l	8.84	<0.018
Methoxychlor Reduction, %	–	>99.8
Carbaryl, mg/l	30.0	0.59
Carbaryl Reduction, %	–	98.0
Malathion, mg/l	93.1	0.13
Malathion Reduction, %	–	99.9
COD, g/l	110	5.15
COD Reduction, %	–	95.3
BOD_5, mg/l	41,000	2,530
BOD_5 Reduction, %	–	93.8
BOD_5/COD	0.37	0.49
DOC, mg/l	26,600	1,040
DOC Reduction, %	–	96.1
pH	2.0	4.4
Total Solids, mg/l	8,090	740
Total Ash, mg/l	1,110	460
Total Volatile Solids, mg/l	7,980	280
Soluble Chloride, mg/l	384	186
Soluble Fluoride, mg/l	<0.5	<0.5

Table 4-3E

WET AIR OXIDATION DEMONSTRATION
PESTICIDE WASTE CLASS

Process Off-Gas Analysis

Carbon Dioxide	14.2%
Oxygen	3.5%
Nitrogen	79.0%
Carbon Monoxide	0.7%
Methane	61.9 ppm
Total Hydrocarbons	153 ppm as methane

F. SOLVENT STILL BOTTOMS WASTE CLASS

SUMMARY

COD, BOD, and DOC removals of 72.3, 73.6, and 47.4 percent were observed in a full-scale wet air oxidation demonstration of a solvent still bottoms type wastewater. Relatively high off-gas total hydrocarbon (THC) levels and rapid exhaustion of the gas train carbon adsorption bed indicated significant stripping of volatile organics during the oxidation run.

An eight-hour wet air oxidation demonstration of a solvent still bottoms type wastewater was performed at the Casmalia Resources, Inc., full-scale wet oxidation installation on March 29, 1984. The demonstration was performed as outlined in agreement OPR-54 between Zimpro, Inc., and the State of California Department of Health Services (DHS). This report contains operating conditions and performance results obtained during the wet air oxidation demonstration.

Results and Discussion

Wet air oxidation of a solvent still bottoms type waste was evaluated in a full-scale demonstration at Casmalia Resources, Casmalia, California, on March 29, 1984. The wastewater was processed continuously during the eight-hour wet air oxidation demonstration.

During the demonstration period, the wet air oxidation unit was operated at an average reactor temperature of 514°F (268°C), a compressed air flow rate of 190 SCFM, and a reactor pressure of 1,550 psig. Waste was processed at an average liquid flow rate of 5.1 GPM, resulting in a nominal residence time of 118 minutes. Residual oxygen concentrations in the process off-gas averaged 3.8 percent during the demonstration period. Feed and effluent composite samples were prepared by combining hourly grab samples from each sampling point.

Analyses of the composite feed and effluent samples are reported in Table 4-1F. COD, BOD, and DOC reductions of 72.3, 73.6, and 47.4 percent were observed.

During the demonstration run, a tendency to strip volatile organics into the gas phase was apparent. The vapor phase activated carbon adsorption bed was rapidly exhausted and relatively high off-gas THC levels were observed. This stripping may have led to the low DOC reduction compared to the COD and BOD reductions. Much of the volatile organic material stripped from the reactor by the gas stream would have recondensed upon cooling in the process heat exchanger. Many of these volatile compounds may have been only partially oxidized because of their short residence time at oxidation temperatures. Partial oxidation would lead to a decrease in oxygen demand for these organics, but not as great a decrease in organic carbon content. Organics which were partially oxidized would also be more likely to recondense because of higher water solubility generally seen for oxygenated organic species.

Soluble chloride analyses for feed and effluent indicated 7,860 and 505 mg/l, respectively. These data indicate material in the feed causing a positive interference in the chloride analysis. Oxidation of this material resulted in an apparent decrease in soluble chloride. This behavior is frequently seen in the wet air oxidation of industrial wastes.

Soluble fluoride increased from 7.5 to 42.7 mg/l upon oxidation, likely due to the destruction of fluorinated organic compounds. This fluoride content was not observed in previous bench scale screening of this wastewater. Fluoride levels much higher than this may not be acceptable in the Casmalia wet air oxidation unit because of corrosive effects on titanium system components.

Results of gas chromatographic analyses of a process off-gas grab sample collected during the wet air oxidation demonstration are shown in Table 4-2F. Carbon dioxide, oxygen, nitrogen, and carbon monoxide concentrations of 11.8, 3.8, 81.2, and nil percent, respectively, were observed. THC and methane concentrations of 217 ppm (expressed as methane) and 80 ppm, respectively, were determined for the process off-gas sample. However, on-line off-gas THC measurements indicated increasing THC concentrations throughout the demonstration run as the vapor phase activated carbon adsorption bed became exhausted.

Table 4-1F

WET AIR OXIDATION DEMONSTRATION
SOLVENT STILL BOTTOMS WASTE CLASS

Wet Air Oxidation Conditions:

Oxidation Temperature	515°F
Nominal Residence Time	118 min.
Waste Flow Rate	5.1 GPM
Compressed Air Flow Rate	190 SCFM
Reactor Pressure	1,550 PSIG
Residual Oxygen Concentration	3.8%

Sample Description	Composit Influent Raw Waste	Composit Influent Oxidized Waste
COD, g/l	166	45.9
COD Reduction, %	–	72.3
BOD_5, mg/l	83,000	21,900
BOD_5 Reduction, %	–	73.6
BOD_5/COD	0.50	0.48
DOC, mg/l	15,200	7,990
DOC Reduction, %	–	47.4
pH	12.5	8.2
Total Solids, mg/l	38,600	30,000
Total Ash, mg/l	25,500	19,800
Total Volatile Solids, mg/l	13,100	10,200
Soluble Chloride, mg/l	7,860	505
Soluble Fluoride, mg/l	7.5	42.7

Table 4-2F

WET AIR OXIDATION DEMONSTRATION
SOLVENT STILL BOTTOMS WASTE CLASS

Process Off-Gas Analysis

Carbon dioxide	11.8%
Oxygen	3.8%
Nitrogen	81.2%
Carbon Monoxide	Nil
Methane	80 ppm
Total Hydrocarbons	217 ppm as methane

SECTION 5

AIR RESOURCES BOARD'S EVALUATION TEST CONDUCTED ON A WET AIR OXIDATION PROCESS TO TREAT HAZARDOUS WASTES

INTRODUCTION

The California Air Resources Board (ARB) conducted six evaluation tests on a wet air oxidation unit manufactured by Zimpro, Inc. As it is mentioned in Section 4, the unit designed to treat toxic wastes, is installed and operated at a Class I waste disposal facility managed by Casmalia Resources and located in Casmalia, California. The test results of the four category wastes, namely—phenols, sulfides, acid organics, and cyanides—are discussed in this report.

The ARB evaluation tests were initiated in response to a request by Santa Barbara County Air Pollution Control District for emission data with which to properly establish and assess the wet air oxidation unit's waste processing capabilities and the effectiveness of the air pollution control devices.

Process Description

1. Wet Air Oxidation System

The wet air oxidation process is a method of oxidizing organic matter suspended or dissolved in water. The principal components of the treatment process and the air pollution control system are shown in Figure 5-1.

Six types of wastes are scheduled to be treated at the facility:

a. Cyanide wastes.

b. Solvent still bottom wastes.

c. Phenolic wastes.

d. Sulfide wastes.

e. Acid-organic wastes.

f. Pesticide wastes.

Each waste type is stored in fixed-roofed tanks located adjacent to the wet air oxidation building. The maximum delivery rate of waste to the treatment building is ten gallons per minute (gpm). Typical process flow rates are between five gpm and eight gpm.

Before being fed into the reaction vessel, the pressure in the line carrying raw, untreated liquor is boosted to approximately 1,800 pounds per square inch gauge (psig) by high pressure pumps. The system is rated at 2,000 psig. After pressurization, the untreated liquor is preheated by a heat exchanger that utilizes the high temperature exit liquid from the reaction vessel. If required, the final process temperature of approximately 500-540°F is attained by a second heat exchanger that uses hot oil on the shell side. Under normal operating conditions, the second heat exchanger is not utilized because sufficient heat energy is extracted from the reaction vessel's effluent to obtain the target process temperatures in the first heat exchanger. However, the second heat exchanger is usually needed for start-up operation. Two compressors introduce ambient air into the raw liquor process line to provide the oxygen necessary to carry out the reaction. This amount is near stoichiometric and is calculated from the chemical oxygen demand (COD) of the waste stream to be treated.

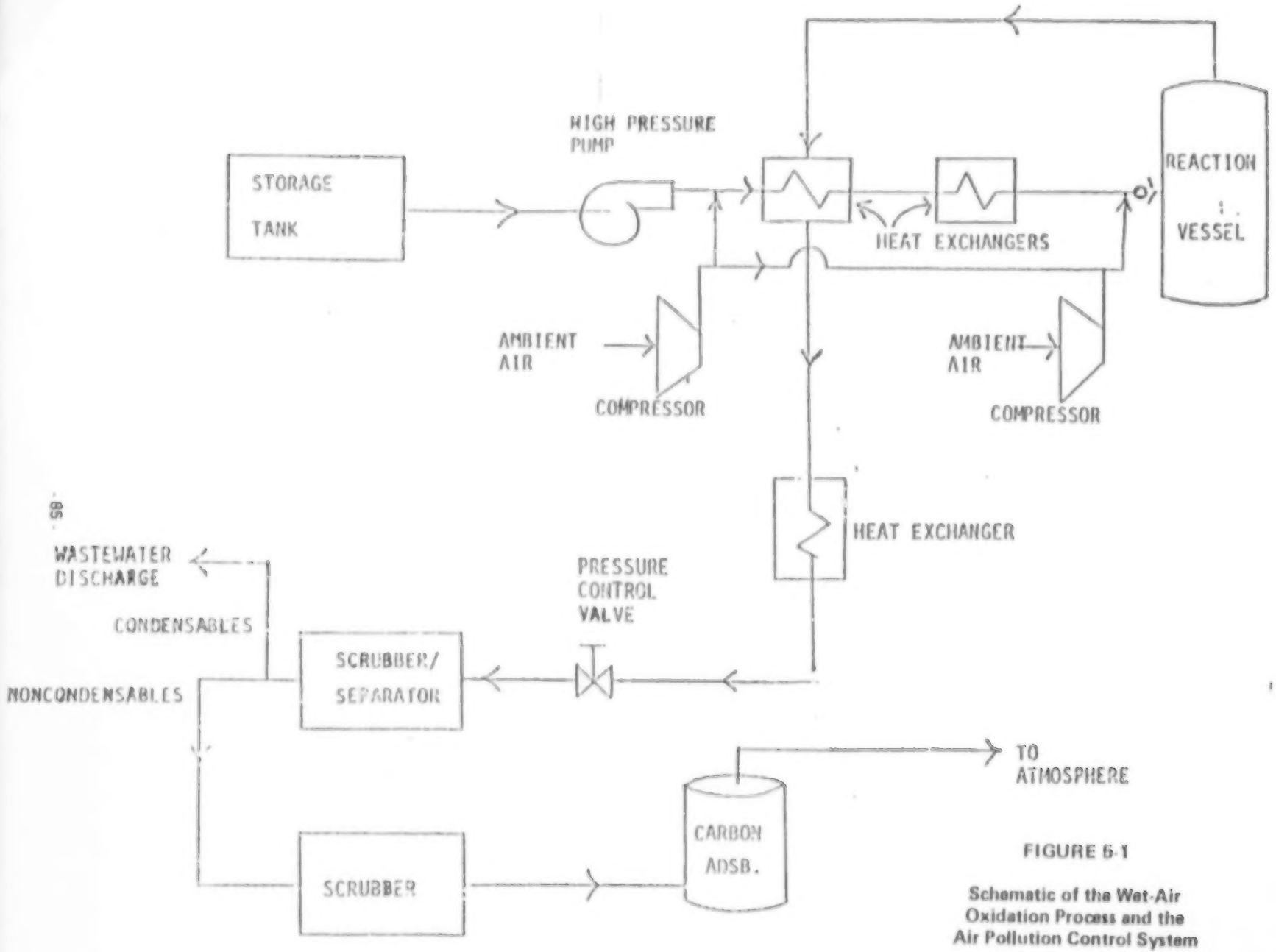


FIGURE 6-1

Schematic of the Wet-Air Oxidation Process and the Air Pollution Control System

The reaction vessel has enough capacity to provide a hold-up time of approximately 60 minutes at a maximum system flow rate of ten gpm. At the process temperature and pressure ranges of 500–540°F and 1,300–1,800 psig, the oxidation rate of the aqueous waste-air mixture is almost instantaneous. If the concentration of oxidizable material, or COD, is high enough, a self sustaining reaction can be maintained in the reaction vessel. After treatment, the temperature of the aqueous waste-air stream is reduced in a heat exchanger and the pressure returned to atmospheric through a pressure control valve.

The treated waste stream is then separated into a condensible and noncondensible fraction in the scrubber/separator. The condensible fraction is pumped out of the condensate well to a water discharge pond. The noncondensible fraction is diverted through two water scrubbers and an activated carbon adsorber before being vented to atmosphere.

2. **Zimpro/Casmalia Screening Program .to Determine Candidate Waste for Wet Air Oxidation Treatment**

To determine if a particular waste is suitable for treatment by the waste air oxidation process, it is subjected to an initial screening process: two one-liter samples of the candidate waste are obtained from the generator and shipped to Zimpro's Wisconsin laboratory. Here, acceptance or rejection of the waste's suitability for commercial oxidation is determined by oxidation in a laboratory autoclave. Figure 5-2 outlines Zimpro's general criteria for scrutinizing each candidate waste. After completion of Zimpro's laboratory analysis, Casmalia Resources personnel are informed about the acceptance or rejection of the candidate waste.

If accepted, Zimpro's analytical results are sent to Casmalia Resources and kept in the generator's file at the disposal site. Subsequent waste shipments received from the generator are sampled directly from the hauler's truck upon arrival at Casmalia's disposal facility and analyzed at an on-site laboratory. Casmalia's on-site analysis is compared to Zimpro's laboratory analysis as a compatibility check. If it passes the on-site analytical check, the waste is transferred to a designated fixed roof storage tank adjacent to the treatment building.

As the waste is processed and treated by the wet air oxidation unit, samples of the process stream are taken from specific points in the system and analyzed. Figure 5-3 schematically follows the waste from the gate through its treatment in the wet air oxidation process and illustrates where process samples are taken and the type of analysis performed.

FIGURE 5-2

ZIMPRO's Wisconsin Laboratory Method for Screening
Potential Wastes for Wet-Air Oxidation

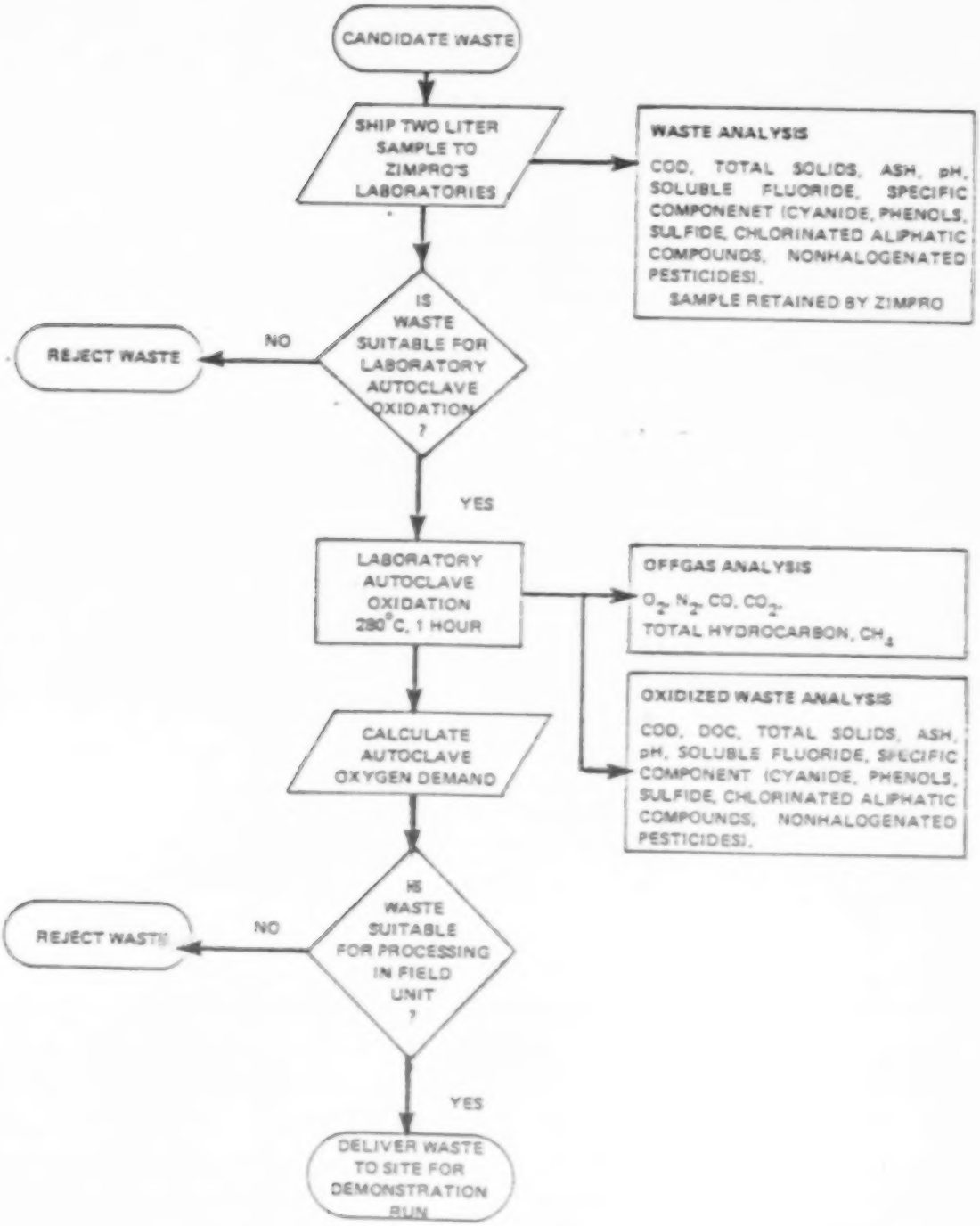
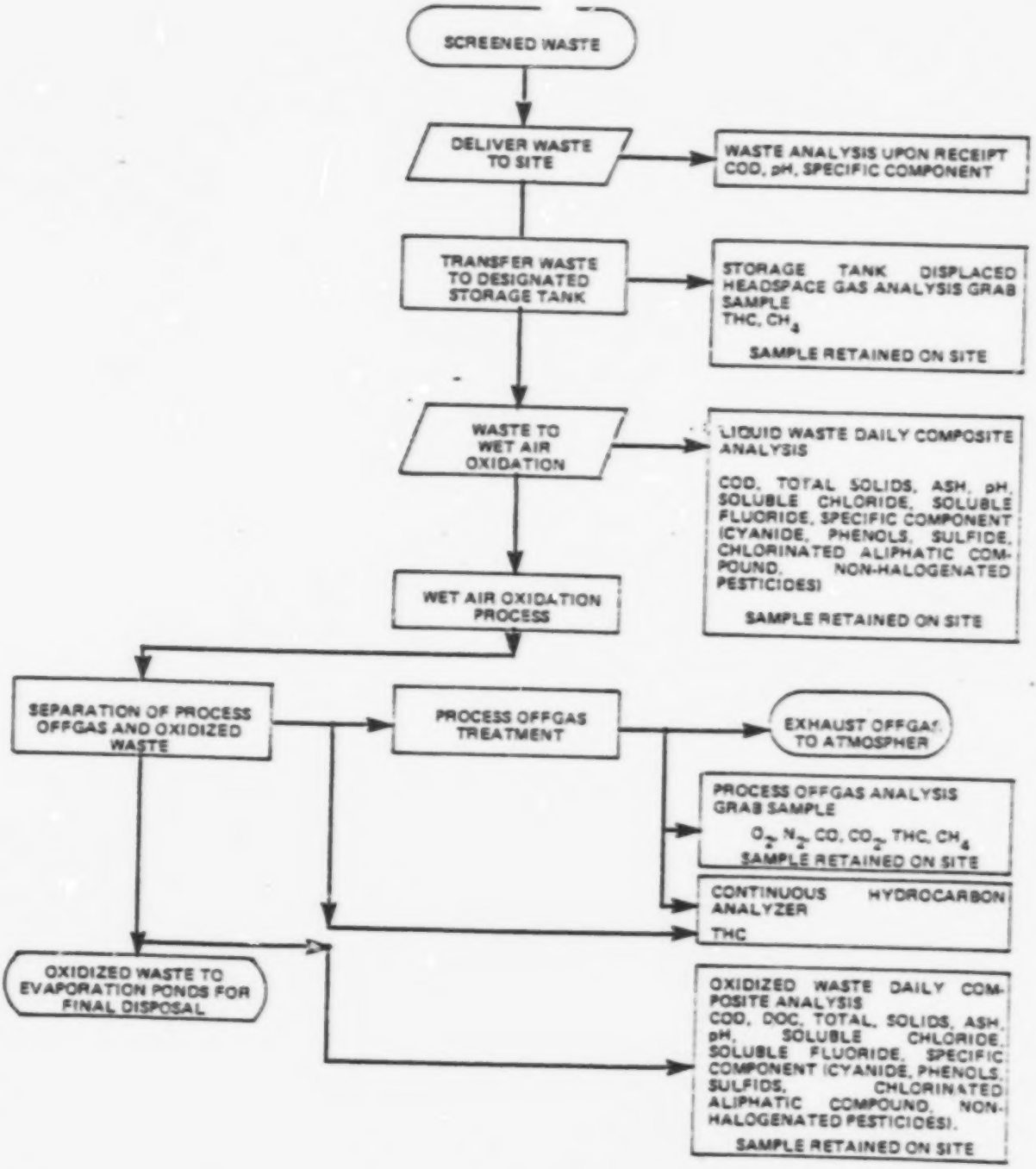

CANDIDATE WASTE
SHIP TWO LITER SAMPLE TO ZIMPRO'S LABORATORIES
WASTE ANALYSIS
COD, TOTAL SOLIDS, ASH, pH, SOLUBLE FLUORIDE, SPECIFIC COMPONENET (CYANIDE, PHENOLS, SULFIDE, CHLORINATED ALIPHATIC COMPOUNDS, NONHALOGENATED PESTICIDES).
SAMPLE RETAINED BY ZIMPRO
IS WASTE SUITABLE FOR LABORATORY AUTOCLAVE OXIDATION ?
NO
REJECT WASTE
YES
LABORATORY AUTOCLAVE OXIDATION 280°C, 1 HOUR
OFFGAS ANALYSIS
O_2, N_2, CO, CO_2, TOTAL HYDROCARBON, CH_4
OXIDIZED WASTE ANALYSIS
COD, DOC, TOTAL SOLIDS, ASH, pH, SOLUBLE FLUORIDE, SPECIFIC COMPONENT (CYANIDE, PHENOLS, SULFIDE, CHLORINATED ALIPHATIC COMPOUNDS, NONHALOGENATED PESTICIDES).
CALCULATE AUTOCLAVE OXYGEN DEMAND
IS WASTE SUITABLE FOR PROCESSING IN FIELD UNIT ?
NO
REJECT WASTE
YES
DELIVER WASTE TO SITE FOR DEMONSTRATION RUN

FIGURE 5-3

ZIMPRO/CASMALIA Resources Process Sampling Locations and Sample Analysis


SCREENED WASTE
DELIVER WASTE TO SITE
WASTE ANALYSIS UPON RECEIPT COD, pH, SPECIFIC COMPONENT
TRANSFER WASTE TO DESIGNATED STORAGE TANK
STORAGE TANK DISPLACED HEADSPACE GAS ANALYSIS GRAB SAMPLE THC, CH_4
SAMPLE RETAINED ON SITE
WASTE TO WET AIR OXIDATION
LIQUID WASTE DAILY COMPOSITE ANALYSIS
COD, TOTAL SOLIDS, ASH, pH, SOLUBLE CHLORIDE, SOLUBLE FLUORIDE, SPECIFIC COMPONENT (CYANIDE, PHENOLS, SULFIDE, CHLORINATED ALIPHATIC COMPOUND, NON-HALOGENATED PESTICIDES)
SAMPLE RETAINED ON SITE
WET AIR OXIDATION PROCESS
SEPARATION OF PROCESS OFFGAS AND OXIDIZED WASTE
PROCESS OFFGAS TREATMENT
EXHAUST OFFGAS TO ATMOSPHER
PROCESS OFFGAS ANALYSIS GRAB SAMPLE
O_2, N_2, CO, CO_2, THC, CH_4
SAMPLE RETAINED ON SITE
CONTINUOUS HYDROCARBON ANALYZER
THC
OXIDIZED WASTE TO EVAPORATION PONDS FOR FINAL DISPOSAL
OXIDIZED WASTE DAILY COMPOSITE ANALYSIS
COD, DOC, TOTAL SOLIDS, ASH, pH, SOLUBLE CHLORIDE, SOLUBLE FLUORIDE, SPECIFIC COMPONENT (CYANIDE, PHENOLS, SULFIDS, CHLORINATED ALIPHATIC COMPOUND, NON-HALOGENATED PESTICIDES).
SAMPLE RETAINED ON SITE

Sampling Methods and Locations

Each waste type treated generates uniquely different liquid and gas phase byproducts. Sampling and monitoring locations are identified in Figure 5-4.

Untreated and treated liquid waste samples were taken in one-pint, glass mason jars and then placed in a cool, dark storage area. At each of these sampling points, numerically identified as 1 and 2 in Figure 5-4, four samples were taken; three grabbed at different times during the test and one composite sample at the conclusion of the test.

The composite samples were generated by combining hourly grab samples into a common container and then taking a sample from this container at the end of the test period. Each composite represented a sample of the process stream entering and leaving the reaction vessel averaged over time.

Inlet and outlet scrubbing water samples, points 6a, 6b, 7a, and 7b, were taken in one-pint, mason jars and stored with the other liquid samples.

Gaseous samples were taken from points 3, 4, and 5, shown in Figure 5-4. This provided the information to determine control equipment efficiency. The sampling train used for cyanide and sulfide/phenol wastes is shown in Figure 5-5. It consists of four modified Greenburg-Smith impingers arranged in series. The first and last impingers are empty and the second and third impingers are each filled with 100 milliliters of 0.1 N sodium hydroxide solution. The potential gas phase organics generated after treatment of the other waste types were captured in tenax and charcoal tubes. The sampling arrangement is illustrated in Figure 5-6.

Process volumetric flow rates to atmosphere were determined using ARB Methods 1 and 2.

Summary and Discussion of Results

1. Wet Air Oxidation Process

A summary of test results is presented in Table 5-1. Wet air oxidation appears to be an effective method for reducing the concentration of liquid phase cyanide and phenol compounds. Cyanide concentrations measured at the inlet and outlet of the wet air oxidation process were

46,300 parts per million by weight (ppm W) and 6.94 ppm W, respectively. Inlet and outlet phenol concentrations were 18,700 micrograms per milliliter (μg/ml) and 2.35 μg/ml. As shown in Table 5-2, the reduction in concentration for both compounds treated by the wet air oxidation process was over 99 percent.

However, wet air oxidation of acid-organics was somewhat less consistent. Two sets of inlet-outlet samples were taken across the process with one indicating a 64 percent reduction of the initial concentration and the other, a 97 percent reduction. Each value was obtained by ratioing the GC/FID generated total peak areas for an inlet-outlet sample pair taken across the wet air oxidation process. When the output sample's GC/FID trace was compared to that for the inlet sample, some peaks had disappeared, some were noticeably reduced, and in some instances, new peaks appeared. Because the availability of standards to identify each peak was limited, the ratio of total peak areas was used to give a relative indication of the wet air oxidation process.

Sulfide reduction across the wet air oxidation process was not measured because of sample related interferences to the laboratory's analytical method. The nature of the interference was unknown and could not be biased out of the analytical procedure.

2. **Condensible, Noncondensible Separator**

With the exception of acid-organics, the amount of noncondensible cyanide, phenols, and sulfide measured at the separator was at the microgram level. Referring to Table 5-1, the quantity of CN, phenol, and sulfide captured was 3.23 μg, and 713 μg, respectively. These values also represent the prescrubbed gas concentrations at the inlet to the scrubber. The total volume drawn for each sample was 45 cubic feet. A "less than" symbol (<) preceeding a value implies that it is below the detection limit of the analytical method with respect to the total volume sampled.

Noncondensible acid-organic samples taken at the separator were used to identify and semi-quantitate the major organic components present in the gas stream prior to entering the control equipment. The results of this work are presented in Table 5-4 and show that for the treatment of this particular waste, halogenated (bromo-, chloro-) alkenes and benzene appear to be the major compounds in the gaseous effluents from the separator.

3. Scrubber

The scrubber was effective in removing sulfide from the gas stream but did not afford any greater control advantage for cyanide and phenols than was achieved by the wet air oxidation process. The results of scrubber inlet and outlet sample analysis are shown in Table 5-3.

Gas phase phenols were not detected at the scrubber inlet or outlet.

The calculated cyanide concentration at the inlet was very low, 0.0025 μg/l or 0.0034 ppm.

The measured scrubber efficiency for controlling noncondensible sulfide was 93.4 percent. The scrubber reduced the inlet concentration of 0.555 μg/l, or ppm, to 0.037 μg/l, or ppm.

The outlet cyanide concentration of 0.0026 μg/l, <0.0025 ppm is comparable to the inlet concentration and indicates that the scrubber has no apparent effect on cyanide when this compound is introduced into the scrubber at such low levels.

It appears that a major portion of the residual phenols and cyanides remaining after the wet air oxidation process is retained in the separator's liquid phase and pumped to the facility's water discharge pond. Any liquid phase reactions that may be occurring are unknown. There is a minimal contribution of cyanide and phenols to the gas phase for control by the scrubber. However, whether the scrubber would be an effective control device at higher inlet concentrations of cyanide and phenols, as might occur during an upset condition, is yet to be determined.

4. Carbon Bed

The carbon bed was most effective in controlling the discharge to atmosphere of gas phase brominated compounds. The inlet concentration of 450 ppm was reduced to 0.18 ppm at the outlet of the carbon bed, representing a removal efficiency of over 99 percent. Note that these concentration values are order of magnitude estimates based on (a) the qualitative speciation data that identified brominated hydrocarbons as the major noncondensible hydrocarbons present and (b) quantitative analysis that normalized all significant GC peaks to 1,2-dibromethane, which was the major identifiable compound for which a standard was available. The normalization technique was performed because standards were not available for the other major peaks. A comparison of these values will give a relative efficiency performance of the carbon adsorber.

The percentage control for cyanide and sulfide was minimal: 17.8 percent and 26.8 percent, respectively. Phenols were not detected in the gas phase.

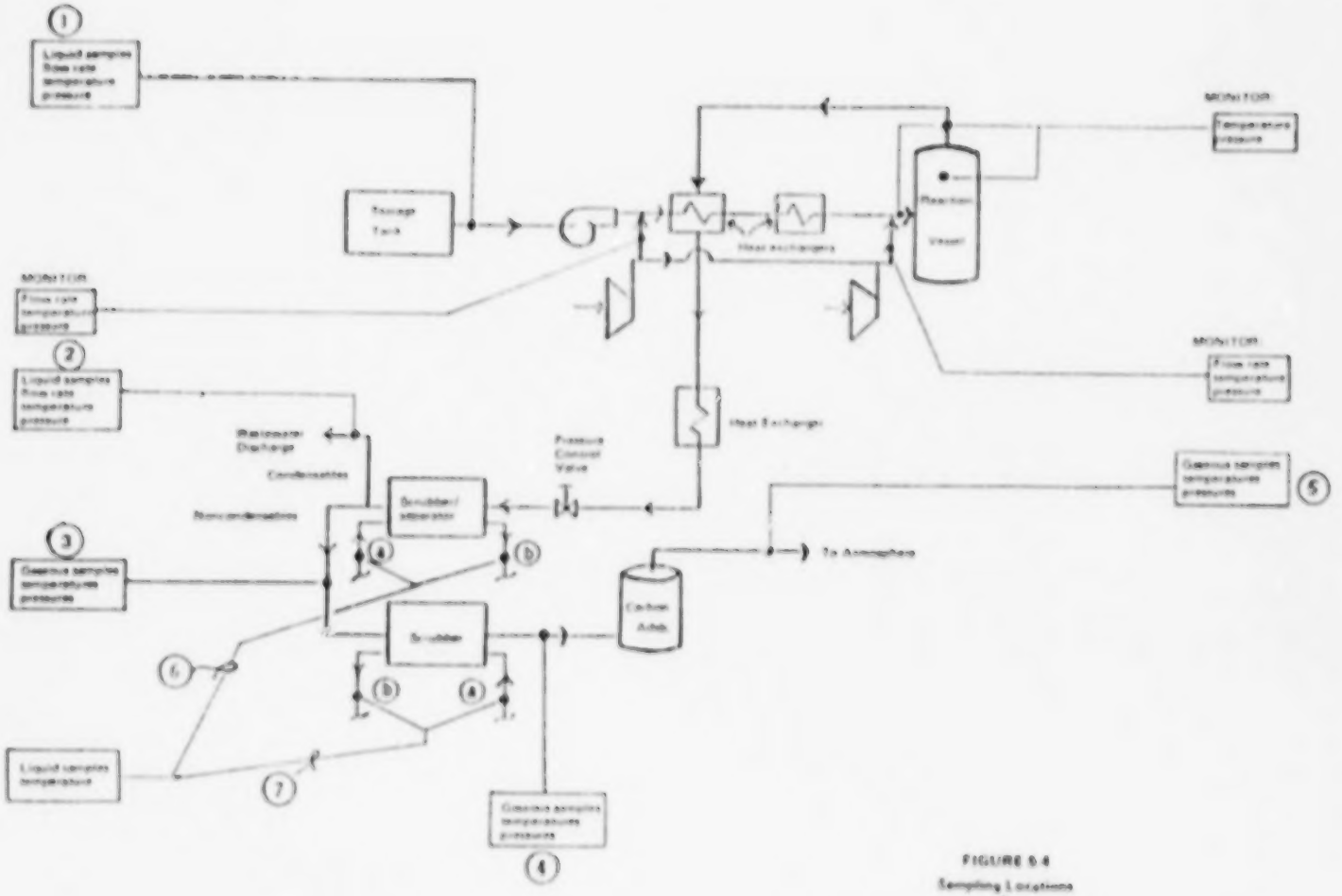


FIGURE 5.4
Sampling Locations
&
Sample Parameters

FIGURE 5-5

Sampling Train for Gas Phase Cyanide, Sulfide, & Phenols

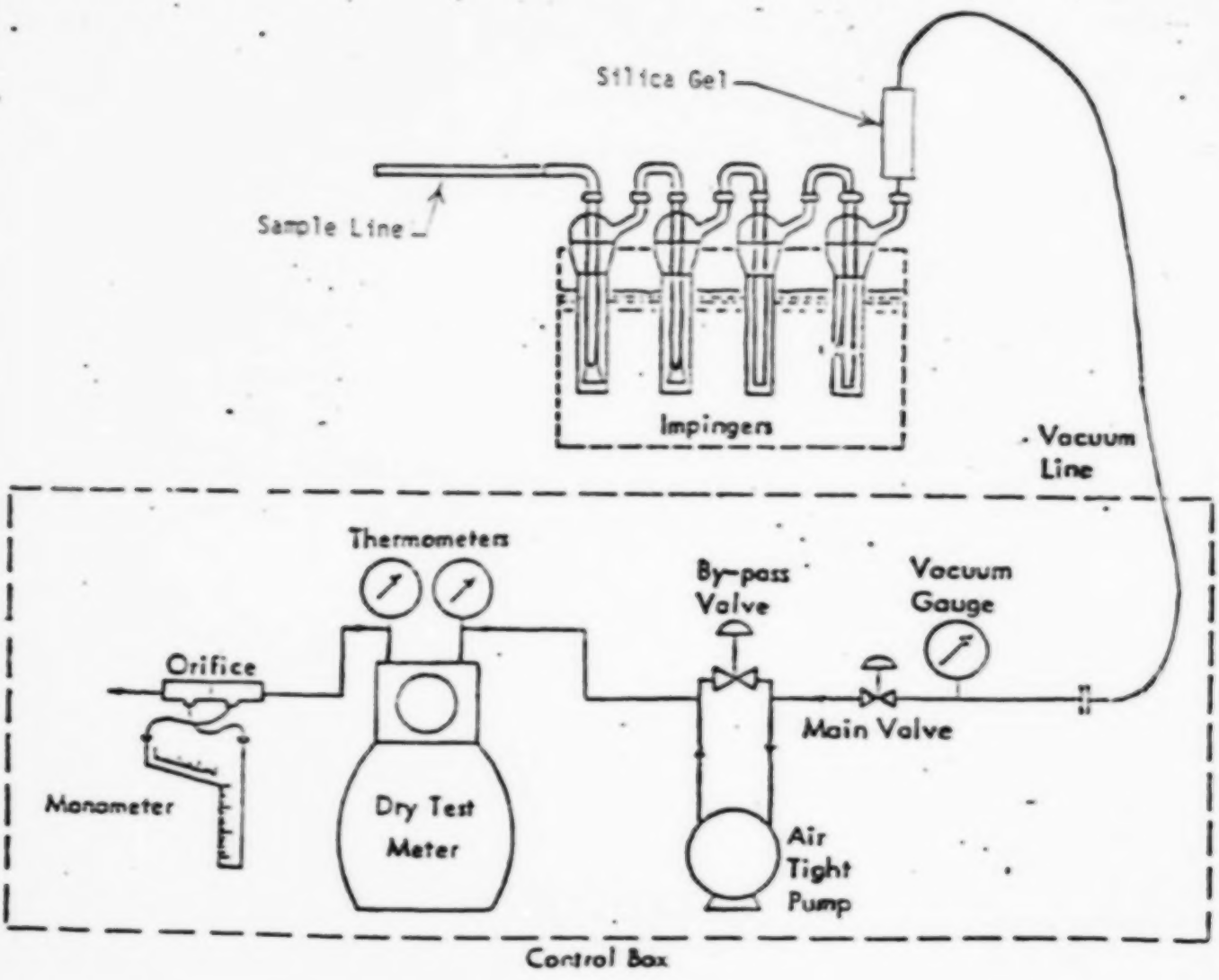


FIGURE 5-6

Sampling Train for Gas Phase Organics

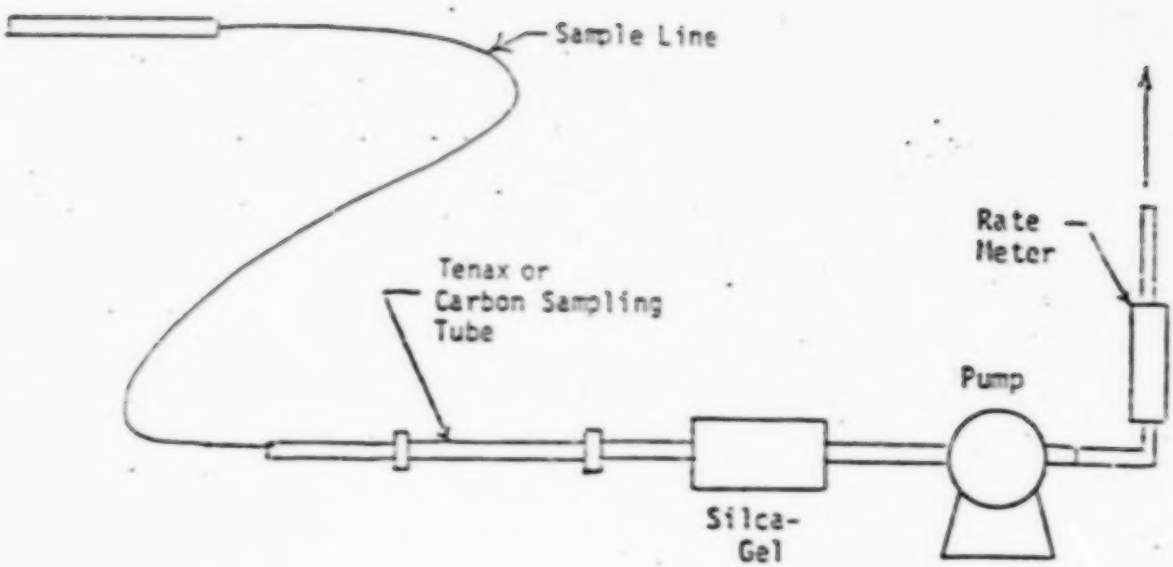


Table 5-1

SUMMARY OF ARB TEST RESULTS

Compound	Sampling Location	Phase of Treatment Process	Concentration	Mass Rate[a] (μg/hr)
CN	1	Untreated Liquid Waste	46,300 ppmW (pH - 13.1)	–
	2	Treated Liquid Wate	6.94 ppmW (pH - 13.1)	–
	3	Pre-Scrubbed Gas	3.37 μg[b]	13.7
	4	Scrubbed Gas	3.37 μg[b]	14.3
	5	Filtered Gas	2.77 μg[b]	11.8
	6	Scrubber Water	None Detected	–
	7	Scrubber Water	None Detected	–
Phenols	1	Untreated Liquid Waste	18,700 μg/ml	–
	2	Treated Liquid Waste	2.35 μg/ml	–
	3	Pre-Scrubbed Gas	<30 μg[b,c]	<127.3
	4	Scrubbed Gas	<30 μg[b,c]	<127.3
	5	Filtered Gas	<30 μg[b,c]	<127.3
	6	Scrubber Water	None Detected	–
	7	Scrubber Water	None Detected	–
Sulfide (As Sulfate)	3	Pre-Scrubbed Gas	713 μg[b]	3,026.3
	4	Scrubbed Gas	47.33 μg[b]	200.9
	5	Filtered Gas	34.67 μg[b]	147.2
Acid-Organics	1	Untreated Liquid Waste	See Table 5-2	–
	2	Treated Liquid Waste	See Table 5-2	–
	3	Pre-Scrubbed Gas	Tenax tubes used to identify and semiquantitate the major components. Analysis by GC/MS.	–
	4	Scrubbed Gas	450 ppm Brominated Compounds	–
	5	Filtered Gas	0.18 ppm	–

a Mass Rate (μg/hr) = $\frac{\text{Mass of Compound Sampled}}{\text{Volume Sampled}}$ x (Volume Flow Rate).

b Total Volume Sampled = 45 ft^3 (1,274.2 Liters).

c Below the detection limit of the analytical method with respect to the total volume sampled.

Table 5-2

PERCENT REDUCTION IN CONCENTRATION ACROSS THE REACTION VESSEL

Compound	Concentration		Percent Reduction[1]
	Inlet	Outlet	
CN	46,300 ppm V	6.94 ppm V	99.99
Phenols	18,700 µg/ml	2.35 µg/ml	99.99
Acid-Organics[2]	–	–	64
	–	–	97

1 Percent Reduction = $\frac{(\text{Inlet}) - (\text{Outlet})}{(\text{Inlet})}$

2 Percent reduction obtained by rationing the GC/FID generated total peak areas for an inlet-outlet sample pair taken across the reaction vessel.

Table 5-3

PERCENT REDUCTION IN CONCENTRATION
ACROSS THE SCRUBBER AND CARBON BED

Compound	Control Device	Concentration		Percent Reduction
		Inlet	Outlet	
CN	Scrubber	3.23 µg	3.37 µg	–
	Carbon Bed	3.37 µg	2.77 µg	17.80
Penols	Scrubber	<30 µg	<30 µg	–
	Carbon Bed	<30 µg	<30 µg	–
Sulfide	Scrubber	713 µg	47.33 µg	93.36
	Carbon Bed	47.33 µg	34.67 µg	26.75
Acid-Organics	Carbon Bed	~ 450 ppm	~ 0.18 ppm	99.96

Table 5-4

NONCONDENSIBLE HYDROCARBONS DETECTED IN THE GASEOUS EFFLUENTS FROM THE SEPARATOR

Compound	Sample	Blank
a Bromochloroethene	M	–
CIS & Trans–Dibromoethenes	M	tr
Two Dibromochloroethenes	M	tr
Tribromoethene	M	m
Tetrabromoethane	M	–
Bromobenzene	M	m
Bromochlorobenzenes	M	m
Acetone	m	M
Two Bromodichloroethenes	m	–
a Dibromodichloroethene	m	tr
Chlorobenzene	m	tr
A Dichlorobenzene	m	tr
Dibromobenzenes	m	tr
a Bromodichlorobenzene	tr	–
a Dibromochlorobenzene	tr	–
Tribromochlorobenzene	m	–
Dichloromethane	–	tr
a Dichloroethene	tr	–
C5 C11 Alkanes	m	m
Three Aldehydes (C5, C6, and C7)	–	tr
Benzene	m	tr
Toluene	tr	m
Ethylbenzene and Xylenes	–	tr
Styrene	–	tr
C3 and C4 Alkylbenzenes	–	m
C4 Alkenylbenzenes	–	tr
Napthalene	–	m
Carbon Disulfide	–	tr
Isopropanol	–	tr
Cyanogene Bromide (possibly)	tr	–
Cyanobutadiene (possibly)	tr	–
Dimethyl Sulfonyl (possibly)	–	tr

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